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Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto

Radionuclide Migration Parameters for the Geosphere

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SAFETY CASE FOR THE DISPOSAL OF SPENT NUCLEAR FUEL AT OLKILUOTO - RADIONUCLIDE MIGRATION PARAMETERS FOR THE GEOSPHERE

Tiivistelmä – Abstract

This report presents an updated radionuclide sorption database for the far-field of the Olkiluoto nuclear waste disposal site.

The geochemical environments are based on site investigations of the present conditions and on modelled evolution of the geosphere. Sorption was estimated to four rock types and on clays, kaolinite and illite, that are common on fracture surfaces in the Olkiluoto site. The possible intrusion of shallow oxidising waters to bedrock was taken into account by estimation of sorption of the redox-sensitive radionuclides in addition to the present anaerobic conditions in oxic modifications of the glacial, fresh and saline waters. The best estimate and the lower limit values were derived to radionuclides that are considered in the safety case of the disposal of spent UO_2 fuel.

The speciations and solubilities of the radionuclides in the water were calculated using the ThermoChimie 7b geochemical database by ANDRA and the PHREEQC code. The ThermoChimie database was complemented with data for new complexes of radionuclides for the comparison of speciation with experimental sorption values, or because the results of experimental speciations in natural waters or a better fit of modelled sorption to experimental data were achieved including these complexes. The speciation and solubility calculations of beryllium were made using the MINTEQ database.

The experimental in-house sorption data from the University of Helsinki for Olkiluoto rocks from the site investigation period, as well as the new data produced for this report, were preferred as the source data. In-house data for rocks and water from the other sites studied during the site investigation period by Posiva were also used. Literature on sorption data to well-defined materials, especially clays, and experiments were used to complement the other data and when no in-house data was available. Sorption of chemical analogues was used for the derivation of sorption values to the radionuclides for which there were no relevant experimental data.

The experimental sorption data to rocks consisted of distribution coefficients to crushed rocks. Conversion of these sorption values to distribution coefficients for intact rock was based on the results of the mineral-specific sorption of radionuclides in diffusion experiments and in sorption to rock surfaces. All these indicate that the mica minerals and other high CEC or high surface area minerals dominate in sorption to intact rock. In this report, sorption to intact rock was taken to take place only to the micaeous minerals and hornblende. Sorption to crushed rock was conservatively assumed not to be mineral-specific. The conversion factors for crushed rock to intact rock were the ratios of the specific surface areas of the micaeous minerals and hornblende to the surface areas of the crushed rocks. Sorption of radionuclides by cation exchange was estimated by model calculation regarding biotite only or based on the estimation of the proportion of sorption to biotite in the crushed rock.

For the clays, the best estimate for the accessibility of the sorption capacity in the intact clays was taken to be the same as that for the dispersed clays used in the experiments.

Avainsanat - Keywords
Sorption, Radionuclides, Far-Field, Olkiluoto

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TURVALLISUUSPERUSTELU KÄYTETYN POLTTOAINEEN LOPPUSIJOITUKSESTA OLKILUOTOON: RADIONUKLIDIEN KALLIOPERÄKULKEUTUMISEN PARAMETRIT

Tiivistelmä – Abstract

Tämä raportti sisältää uudistetun tietokannan radionuklidien sorptioparametreistä kaukoalueella Olkiluodon kallioperässä.

Tarkasteltavat geokemialliset olosuhteet perustuvat Olkiluodon paikkatutkimuksissa todettuihin nykyisiin olosuhteisiin sekä malleilla laskettuihin tuleviin olosuhteisiin. Radionuklidien sorptio arvioitiin neljälle kivilajille sekä rakopinnoilla Olkiluodossa yleisille saville. Mahdollinen hapellisten vesien tunkeutuminen kallioperään otettiin huomioon tarkastelemalla redox-herkkien aineiden sorptiota myös potentiaalisesti aerobisissa vesissä. Sorptioparametreille arvioitiin sekä ilmeisin arvo että alaraja-arvo.

Radionuklidin kemialliset muodot vesissä sekä liukoisuus laskettiin käyttäen ANDRA:n kehittämää Thermo_Chimie 7b -tietokantaa ja geokemiallista PHREEQC-malliohjelmaa. Thermo_Chimie-tietokantaa täydennettiin kirjallisuudesta saaduilla uusimmilla parametriarvoilla, jotka on todettu tärkeiksi luonnon vesiä analysoimalla ja joiden avulla kokeellinen sorptio ja laskennallinen sorptio ovat aiempaa paremmin saatu yhteensopiviksi.

Sorption arvioinnin lähtötietoina käytettiin ensisijaisesti Helsingin yliopiston Radiokemian laboratoriossa Olkiluodon kiville ja vesille saatuja tuloksia sekä Posiva Oy:n paikkatutkimusvaiheessa saatuja muita sorptiotuloksia. Näitä täydennettiin tämän raportin teon aikana Radiokemian laboratoriossa tehtyjen kokeiden tuloksilla sekä kirjallisuudessa hyvin kuvattujen kokeiden tuloksilla, erityisesti saville määritetyillä arvoilla. Muun tiedon puuttuessa radionuklidin sorptio arvioitiin sen kanssa kemiallisesti samankaltaisen aineen sorptiosta.

Kivimateriaaleille on tehty kokeita pääasiassa käyttäen murskattuja kiviä. Murskeille saatujen sorptioarvojen muuttaminen ehjille kiville perustui sekä jo aikaisemmin diffuusiokokeissa että kivipinnoille saatuihin tuloksiin, joiden mukaan radionuklidit sorboituvat valtaosin kiven kiillemineraaleihin sekä muihin suuren kationin-vaihtokapasiteetin omaaviin ja huokoisiin suuren pinta-alan mineraaleihin. Tässä raportissa sorptioarvojen muuttaminen murskeelle saadusta arvosta ehjälle kivelle tehtiin olettamalla, että murskeessa kaikki mineraalipinnat sorboivat samalla tehokkuudella, mutta ehjässä kivessä sorptio tapahtuu vain kiillemineraalehin ja sarvivälkkeeseen. Muut mineraalit oletettiin sorboimattomiksi. Sorptioarvon muuntokertoimena käytettiin kiillemineraalien ja sarvivälkkeen kokonaispinta-alan ja kivimurskeen ominaispinta-alan suhdetta. Vain kationivaihdolla sorboituvien alkali- ja maa-alkalikationien sorptio joko laskettiin sorptiomallilla tai perustui arvioon biotiitin osuudesta murskatulle kivelle mitatusta sorptiosta.

Saville ilmeisimmän sorptioarvon arvioinnissa oletettiin kirjallisuudessa esitettyihin tuloksiin perustuen, että sorptio ehjälle savelle on sama kuin kokeissa käytetylle hienojakoiselle savelle.

Avainsanat - Keywords
Sorptio, radionuklidit, kaukoalue, Olkiluoto

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ABBREVIATIONS

API	American Petroleum Institute
BET (BET/N_2)	surface area determined by nitrogen gas adsorption
CAT	cationic charge concentration
CEC	cation exchange capacity
DDL	double diffuse layer
DOC	dissolved organic carbon
EPA	Environmental Protection Agency, United States Office Of Air and Radiation
FSS	fraction of sorbed species
GW	groundwater
HTO	tritiated water
HU	University of Helsinki, Laboratory of Radiochemistry
ICP-MS	inductively coupled mass spectrometry
IS	ionic strength
JNC SDB	sorption database from Japan Nuclear Cycle Development Institute (now Japan Atomic Energy Agency, JAEA)
KBS-3H	disposal method with long horizontal deposition drifts
K_d	mass distribution ratio of element (nuclide) for, e.g., intact rock and clay
Ki	Kivetty
LFER	Linear Free Energy Relationship
LLD	lower limit of determination
Ln(III)	lanthanide
LSC	liquid scintillation counter
MINTEQ v.4	thermodynamic database in PHREEQC
NEA TDB	thermodynamic database from Nuclear Energy Agency
OL	Olkiluoto
PHREEQC	a geochemical modelling programme
PZC	point of zero charge
R_a	experimental value of surface sorption distribution ratio of element (nuclide)
R_d	experimental value of mass distribution ratio of element (nuclide)
REF	pH of reference water
R_{max}	R_d value based on counting error addition
R_{min}	R_d value based on counting error subtraction
RN	radionuclide
Ro	Romuvaara
S(%)	sorption percentage
SA	surface area
SD	source data rock
SDB	sorption database
SOH_2^+	positively charged variable charge sorption site
SUM	sum of mineral (biotite+chlorite+muscovite+sericite +hornblende) contents
TDB	thermodynamic database

TDS	total dissolved solids
TIC	total inorganic carbon
UF	uncertainty factor
X, Xa, Xb site	cation exchange site of biotite

Rocks

1-YSP-83	Olkiluoto drill core 1-YSP-83 (tonalite)
GD (TON)	Olkiluoto granodiorite
GN	Olkiluoto mica gneiss
GR	Olkiluoto granite
HHGR-6	Hästholmen granite
KiKR1	Kivetty drill core KR1 (granite)
KLX	Laxemar granite
KLX 04	Laxemar granite
KLX02	Swedish Laxemar granite
MGN,MG	Olkiluoto mica gneiss
O2A TON,TON	Olkiluoto tonalite
Ol1MGN	Olkiluoto mica gneiss
Ol2B GR,GR	Olkiluoto granite
OL-A	Olkiluoto granodiorite
OL-B	Olkiluoto mica gneiss
OLKR1	Olkiluoto drill core KR1 (mica gneiss)
OLKR5	Olkiluoto drill core KR5 (mica gneiss)
OPA	Opalinus clay
P-MIGGN	Olkiluoto P-series migmatic gneisses
T-MIGGN	Olkiluoto T-series migmatic gneisses
PGR	Olkiluoto pegmatitic granite
P-TGG	Olkiluoto P-series tonalite granodiorite granite gneiss
RoGR	Romuvaara granite
ROKR3	Romuvaara drill core KR3 (tonalite)
RoMG	Romuvaara mica gneiss
RoTon	Romuvaara tonalite
T-MGN	Olkiluoto T-series mica gneiss
T-TGG	Olkiluoto T-series tonalite granodiorite granite gneiss

Minerals

CCa-2	chlorite from U.S. Clay Minerals Society
HKGa-1b, HKGA	conditioned kaolinite KGa-1b
IMt-1	illite from U.S. Clay Minerals Society
KGa-1b	kaolinite from U.S. Clay Minerals Society
Min-U-Sil 5	alpha-quartz
OLB-A	biotite separated from OL-A rock
OLB-B	biotite separated from OL-B rock

Waters

ALL, ALLARD	Allard water (synthetic water)
ALLMO	fresh oxic granitic reference water (Modified Allard)

ALLMR	fresh mildly reducing granitic reference water (Modified Allard)
GRIMSEL	Grimsel glacial meltwater
KiKR4	Kivetty drill core KR4 (groundwater)
KR13_362_6	Olkiluoto drill core KR13 groundwater from depth 362 m
KR20_465_1	Olkiluoto drill core KR20 saline groundwater from depth 465 m
KR4_81_1	Olkiluoto drill core KR4 brackish groundwater from depth 81 m
KR6_135_8	Olkiluoto drill core KR6 brackish groundwater from depth 135 m
OLBA	carbonate-containing reducing brackish reference water
OLGA	glacial anoxic meltwater (synthetic water)
OLGO	glacial oxic meltwater (synthetic water)
OLKR11	Olkiluoto drill core KR11 (groundwater)
OLKR12	Olkiluoto drill core KR12 (groundwater)
OLKR5	Olkiluoto drill core KR5 (groundwater)
OLKR6	Olkiluoto drill core KR6 (groundwater)
OLPVA2, PVA2	Olkiluoto PVA groundwater, from brackish groundwater sampling station PVA2 in the VLJ-repository
OLSO	saline oxic reference water (synthetic water)
OLSR	saline reducing reference water (synthetic water)
YD1	Olkiluoto YD1 groundwater

FOREWORD

This report was prepared under contract to Posiva Oy. The contact person at Posiva Oy was Marja Vuorio. Pirjo Hellä and Margit Snellman were the contact persons at Saanio & Riekkola Oy.

The report was reviewed as an early draft by Michael Ochs (BMG Engineering Limited) and Martin Glaus (Paul Scherrer Institut). We thank Ignasi Puigdomenech (Swedish Nuclear Fuel and Waste Management Co) for critical discussions during the review. A later version of the report was reviewed by Professor Jukka Lehto (Laboratory of Radiochemistry), Paul Wersin and Mirjam Kiczka (Gruner AG) and Marja Vuorio (Posiva Oy).

The English language was checked by Aakkosto Oy.

TABLE OF CONTENTS

1 INTRODUCTION

Used nuclear fuel from the Olkiluoto and Loviisa power plants is planned to be disposed of in a repository constructed in the Olkiluoto bedrock. This updated database includes sorption parameters for the reference rocks in the reference groundwater conditions. Sorption of waste nuclides is described in the POSIVA spent fuel safety assessment by using values of the mass distribution ratio K_d. Before this report, K_d values were surveyed for the Olkiluoto geosphere in Hakanen & Hölttä (1992), applied in the TVO-92 safety assessment (Vieno et al. 1992) and used with minor changes in the TILA-96 (Vieno & Nordman 1996), TILA-99 (Vieno & Nordman 1999) and KBS-H assessments (Nykyri et al. 2008).

The Olkiluoto bedrock is composed of several rocks (Kärki & Paulamäki 2006). In this report, sorption values of radionuclides are derived for the rocks selected by Posiva: a mica gneiss, two tonalite-granite-granodiorite gneisses and a pegmatitic granite. Sorption values were also derived for common fracture coating clays.

The waters for the evaluation of sorption were selected as suggested by the estimated evolution of groundwaters in Olkiluoto (Pastina & Hellä 2006). The groundwater types were a glacial meltwater, a low salinity mildly reducing water, reducing brackish carbonate-containing waters and reducing saline waters. Sorption in waters affected by dissolved cementitious materials at pH 10 was also estimated. Groundwater simulants were used in new laboratory experiments performed to complement existing sorption data.

The PHREEQC program (Parkhurst & Appelo 1999, Appelo & Post 2008) was used for the calculation of the chemical forms (speciation) and solubilities of the waste nuclides and in the waters. The ThermoChimie Version 7b thermodynamic database (ANDRA 2009) was used and complemented by reports of very new complexation reactions in the available literature. Speciation calculations were undertaken to cover pH ranges larger than the specific pH for the water.

The first priority in the selection of source sorption data was the HU (University of Helsinki, Laboratory of Radiochemistry) in-house data on sorption values, because much of the data was produced for rocks and groundwaters from Olkiluoto. This sorption data for rocks originates to a large extent from the Posiva site-selection investigation period, and also includes sorption data for rocks and waters from the other candidate sites as well as Olkiluoto. This in-house data for the rock materials and solutions needed in the evaluation of experimental R_d values for conversion to K_d values to intact rock is best known to the authors. To complement the in-house sorption data, new sorption experiments using the reference rocks and clays were performed for some nuclides.

A method for the conversion of sorption on crushed rocks to sorption on intact rock is presented. An in-house cation exchange model for the calculation of the sorption of cesium on the rocks was used.

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2 CONDITIONS

2.1 Rocks

The mineral compositions of the reference rocks are given in Kärki & Paulamäki (2006) and the compositions of the rocks selected for this study are given in Appendix 1.

Parts of the cores were crushed to grain size < 2 mm at the Geological Survey of Finland (GSF) for batch type sorption studies to complement the in-house (HU) sorption data from the radiochemistry laboratory. A report on the separation of biotites from Olkiluoto gneisses is included in Appendix 1.

Slab-type samples were cut from the cores for studying sorption to intact rock using electromigration.

2.2 Clays

K_d values are also suggested for common fracture coating clays. Site-specific clays were not available. The clays used in the sorption experiments were source and reference clays KGa-1b kaolinite, IMt-1 illite and CCa-2 chlorite from the U.S. Clay Minerals Society (Appendix 2).

2.3 Waters

The compositions and recipes of the reference groundwaters are described in Appendix 3. Selection of the reference waters is explained in Hellä et al. (2014). Simulants of the groundwaters were used in the laboratory sorption experiments. The compositions of the anaerobic glacial water (OLGA), low salinity mildly reducing water (ALLMR, Vuorinen & Snellman 1998), brackish reducing high carbonate water (OLBA) and saline reducing water (OLSR, Vuorinen & Snellman 1998) are given in Appendix 3, together with the compositions of the aerobic variants of the glacial meltwater (OLGO) and the low salinity (ALLMO) and saline groundwater (OLSO). In the sorption studies performed during the Posiva site selection phase in the 1990s, several natural site-specific ground waters were used. The compositions of these waters are given with the source sorption data for the specific nuclide in the published reports. The site-specific groundwaters contain many trace constituents that are lacking from the simulants. One of these is DOC (dissolved organic carbon) compounds. Complexation of radionuclides with DOC, especially with humic compounds, may significantly lower the sorption on mineral surfaces. This effect is largest to tri-valent cations (Hummel et al. 2000). It is assumed (Pitkänen et al. 2007) that the concentration of DOC in deep groundwaters in Olkiluoto is much lower than that measured, due to contamination from packers and uncertainties in the amounts of hydrocarbons in the analysed waters. The measured DOC concentrations are highest at the shallow depths.

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3 DERIVATION OF K_d FOR INTACT ROCKS AND CLAYS

3.1 Introduction

In this report the mass distribution ratio R_d (m^3/kg) of a nuclide is the experimentally determined value of the ratio of radionuclide concentration in the solid (mol/kg) to the nuclide concentration in the solution (mol/m^3). The K_d value is the equilibrium value for the distribution ratio in the specific conditions. In the literature, K_d is often used instead of R_d to also represent the experimental distribution ratio. In this report, R_d refers to the experimental distribution ratio value of a nuclide.

Sorption experiments for the determination of the mass distribution ratio (R_d) on crystalline rock and primary minerals and clay materials have mostly been conducted using crushed materials. During the crushing of drill core pieces, not only are old grain boundary and other fissure surfaces exposed, but also new mineral surfaces are generated and can take part in sorption in the experiments. To estimate the K_d value for intact crystalline rock, the impact of these new surfaces must be subtracted from the measured sorption. Sorption on intact rock depends on the sorption capacity of the different minerals and accessibility of sorption sites. The sorption on clays is also most often determined for suspended solids. For conversion of sorption on crushed materials to K_d for intact rocks and clays, the need for scaling procedures must be evaluated.

3.2 Sorption mechanisms

Sorption of solutes on mineral surfaces takes place by cation exchange on silicate mineral surfaces that have structural permanent negative charge, and on variable charge surface sites on aluminosilicate and oxide minerals. Cation exchange on permanently negative silicate mineral surfaces at pH 6 and higher is the dominating sorption mechanism for non-hydrolysed cations like alkaline and alkaline earth cations. The structural charge is fully compensated with exchangeable ions in all conditions. Charge balance is assumed in cation exchange reactions. Because the inner parts of mineral grains are inaccessible or only partially accessible to solutes, the measured concentration of exchangeable charge is the accessible cation exchange capacity (CEC). This should preferentially be determined for the cations under study in order to apply the value, e.g. in sorption modelling or comparison of sorption capacity of aluminosilicate materials.

Sorption of hydrolysed species of transition metals, lanthanides and actinides takes place on variable charge surface sites (Dzombak & Morel 1990, Bradbury & Baeyens 2005). Sorption on these sites is often modelled using the surface complexation approach. Typical of this is the dependency of sorption on hydroxo complexation of the solute cation. Sorption of oxoanions has been also modelled by surface complexation (Stumm & Morgan 1996). Sorption of non-complexed anions such as iodide ions takes place on positively charged surface sites. In sorption modelling, the site density (sites/surface area) is often a fixed parameter, and the site concentration is calculated by using the surface area of the mineral or generic solid. As for CEC, the accessible concentration of variable charge sorption sites is larger for a larger surface area of the same solid.

3.3 Derivation K_d for intact rocks and clays

Sorption experiments have indicated the preferential sorption of cesium (Cs^+) and strontium (Sr^{2+}) on micas, but also the sorption of nickel (Ni(II)), europium (Eu(III)), americium (Am(III)) and plutonium (Pu (III/IV)) in groundwater under anaerobic conditions is much higher on micas than on felsic minerals and quartz (e.g. Lindberg et al. 1983, Pinnioja et al. 1984, Koskinen et al. 1988). Pu on a potassium feldspar crystal surface was concentrated on the mica/sericite impurities on the unaltered feldspar (Koskinen et al. 1988). This is due to the high surface area of sericite compared with that of feldspar. Also, uranium, lanthanum and neodymium are sorbed to granitic biotite in a much higher degree than to feldspar and other primary minerals (Berry et al. 1993, 1994, Misaelides et al. 2000). From the above it follows that, in a simplistic approach, for the comparison of sorption to different rocks, the mineralogical properties that make the difference are the accessible CEC and the accessible surface area.

3.3.1 Crystalline rocks

Crystalline rocks in Olkiluoto are composed of heterogeneously dispersed primary minerals of smaller than mm to cm scale grain sizes. The sorption sites in the intact rock are accessible to solutes through pores and fissures of the rock.

The pore structure of Olkiluoto rocks determined using the C-14-PMMA (carbon-14 polymethylmetacrylate) method indicates that in the unaltered rock the porosity of quartz and feldspar grains was low and the more porous parts of a rock were accessible to MMA (methylmetacrylate) solution through grain boundary porosity (Lindberg et al. 2010, Siitari-Kauppi et al. 2010, Kuva et al. 2012). The more porous minerals were micas, altered minerals and clays. In some rocks, the porosity of biotite was lower than the determination limit of the C-14 PMMA method.

In-diffusion experiments on solutes have indicated that in intact unaltered rocks the used tracers were located mainly in the dark minerals like biotite, chlorite and hornblende (Pinnioja et al. 1985, Suksi et al. 1987, Kaukonen et al. 2000, Alonso et al. 2003). These results confirm that the micas in intact rocks are accessible to sorption of solutes that migrate into the rock from the solution in which the rocks are immersed.

An experimental approach for the determination of inner surface areas, cation exchange capacities and K_d values of cesium for crystalline rocks has been studied by André et al. (2008a, 2008b, 2009) for Swedish granites. R_d values of cesium for crushed rocks were up to 30 times higher than those determined by electromigration for intact rock. The difference was approximately threefold when comparing the sorption values calculated for the surface areas of both. It is fairly clear that this kind of ratio depends largely on the mineral composition of the rock and grain size of the crushed rock. It is to be expected that, for mica-poor granites like those used by André et al. (2008a, 2008b, 2009), sorption on crushed rock is much higher than on intact rock.

Cation exchange capacity of rocks

Kyllönen et al. (2008), Huitti et al. (1998) and earlier Pinnioja et al. (1984) have shown that sorption of Cs on crushed rock and on rock surface (thin section) is dominated by

sorption to biotite, and that the surface distribution ratio (R_a) of Cs and Sr for a rock is linearly directly proportional to the proportion of biotite in the rock. This suggests that the CEC values for the unaltered intact rocks depend on the proportion of micas, especially of biotite in the rocks and the accessible CEC for biotite. The proportions of other micas in the gneissic reference rocks are low, or their CEC values are low (and more uncertain), as compared to that of biotite (Huitti et al. 1998, McKinley et al. 2004).

Biotite in Olkiluoto mica gneisses and granodiorites is commonly fine grained, as exemplified in Appendix 1 (Cernet et al. 2005). A CEC value 15 μeq/g for 0.25 – 0.5 mm grain size biotite was determined for biotites (BET surface area 0.8 m^2/g) that were separated from Olkiluoto mica gneisses and tonalites (Tables 4-3 and 4-4 in Kyllönen et al. (2008)) and for biotites from Olkiluoto granodiorite and mica gneiss 1.3 μeq/g (BET surface area 1.0 m^2/g) and 1.6 μeq/g (BET surface area 1.3 m^2/g) (Olin et al. 2006). Torstenfelt et al. (1981) measured CEC of 17 μeq/g to sorption of Na^+ to a very finely-grained biotite. For the <0.1 mm grain size crushed pegmatitic biotite, the CEC was much higher (Appendix B in Kyllönen et al. (2008)).

Literature values of CEC for crystalline rocks are very scarce. The CEC value (0.135 meq/kg) calculated for the Olkiluoto pegmatite granite PGR (0.9 % biotite, 15 μeq/g biotite) is in fair agreement with the CEC (0.05 - 0.14 meq/kg) determined for a Swedish granite (KLX02, 3 % biotite) used in an electromigration experiment in André et al. (2009).

Accessible cation exchange capacity in the reference rocks

Accessibility of cation exchange capacity to Cs (accessible permanent negative charge sorption capacity) in the reference rocks was experimentally surveyed. An electromigration method presented in André (2008a) was applied. The electromigration experiment resembles a through diffusion experiment but the electric field is used to speed up transfer of ions in the rock pores. The potential field 300 – 500 V/m over the rock slice separating the two Cs-spiked 0.1 M NaCl solution reservoirs was used. Cs-concentration in the solutions was followed by the measurements of the radioactive Cs-134 tracer. The experiments were continued until the Cs-concentration in the solution reservoirs was constant. A blind prediction of sorption was made using the cation exchange model for Cs described in Chapter 7. The accessible CEC used in the calculations was 15 μeq/g of biotite. Table 3-1 gives the calculated sorption values to the rocks together with properties of the rock slices. Table 3-1 also gives values for the rapakivi granite slice from Hästholmen that was earlier used in measurement of diffusion of HTO through the rock (Huitti et al. 1996) and that was here used to test the experimental setup.

Sorption on the Olkiluoto rock slices is indicated in Figures 3-1 to 3-5. The experimental sorption values are the same or higher than the calculated values for mica gneiss T-MGN, T-series tonalite-granodiorite-granite-gneiss T-TGG and pegmatitic granite PGR. Experimental sorption to P-series tonalite-granodiorite-gneiss P-TGG slices is slower than to the other rock types. This may be due to the fact that in these gneissic samples the foliation of biotite was parallel to the planar surfaces of the

samples (perpendicular to the electric field) and the migration pathways are longer than in the other rocks. Also, in P-TGG rocks the steady-state sorption values were about 50 % of the calculated average values, regardless of the different thicknesses of the slices. The authors made the conclusion that in the T-MGN, T-TGG and PGR rocks the amount of accessible CEC exceeds the CEC determined for the biotites (15 μeq/g biotite) used in the sorption model parametrisation. In the P-TGG rock, only half of the CEC value (0.5*15 μeq/g biotite) in the biotite was accessible to sorption of Cs. The sorption mechanism of Cs is cation exchange. The above results suggest that there exist in the waters predominantly non-complexed cations, Cs and alkaline earth elements Sr and Ra. The accessible CEC in intact T-MGN, T-TGG and PGR is at least 15 μeq/g of biotite, but for intact P-TGG only half of the CEC derived from amount of biotite is accessible. For the low-biotite rocks, the experimental sorption is much higher than modelled. This indicates that cesium in these rocks was also sorbed to other minerals than biotite.

Table 3-1. *Sorption (%) of cesium on rock slices. Results for electromigration experiment. Experimental sorption (Exp) and modelled sorption values for average (Av), minimum (Min) and maximum (Max) biotite concentrations are indicated. The volumetric porosities derived from water impregnation experiments and thicknesses of the slices are given.*

Rock_sample	Thickness (mm)	Biotite (%)	Porosity (vol %)	Sorption Av (%)	Sorption Min (%)	Sorption Max (%)	Exp (%)
HHGR-6	15	4.2	3.5	48			**92**
T-MGN_2	3.15	21±8	1.88	62	46	72	**80**
T-TGG_7	19.2	8.2±7.5	0.23	80	15	92	**70**
PGR_11	19.0	0.9±1.7	0.40	18	0.01	44	**80**
P-TGG_1	2.80	22.5±7.1	0.23	47	36	57	**25**
P-TGG_4b	16.45	22.5±7.1	0.23	93	87	96	**51**

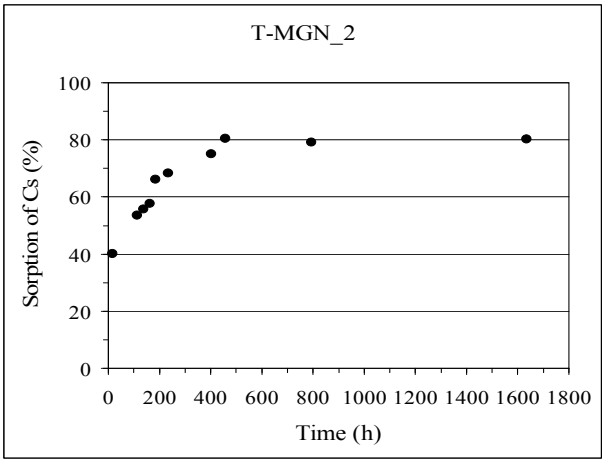

Figure 3-1. *Sorption of Cs on intact T-MGN rock. The voltage used was 9 V.*

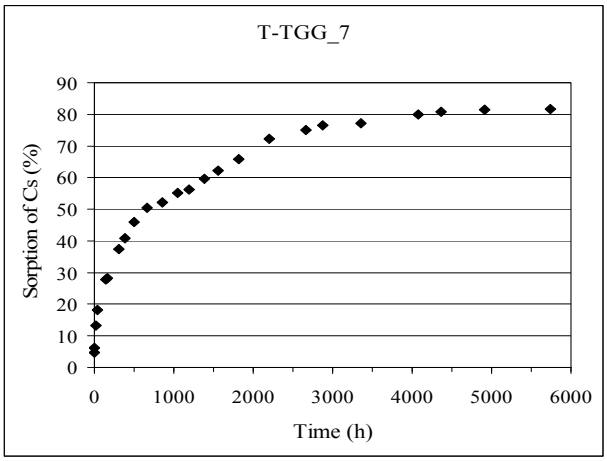

Figure 3-2. *Sorption of Cs on intact T-TGG rock. The voltage used was 9 V.*

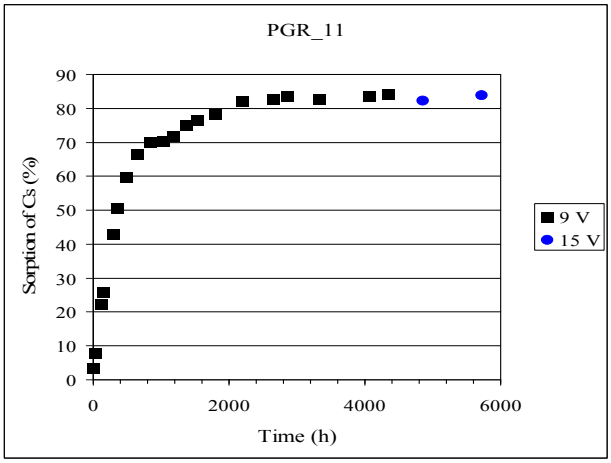

Figure 3-3. *Sorption of Cs on intact PGR rock. The voltages used in the experiments are indicated.*

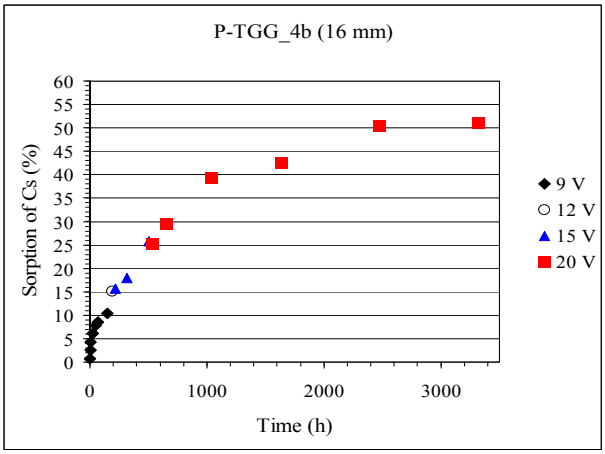

Figure 3-4. *Sorption of Cs on P-TGG gneiss slice 4b. The voltages used in the experiments are indicated.*

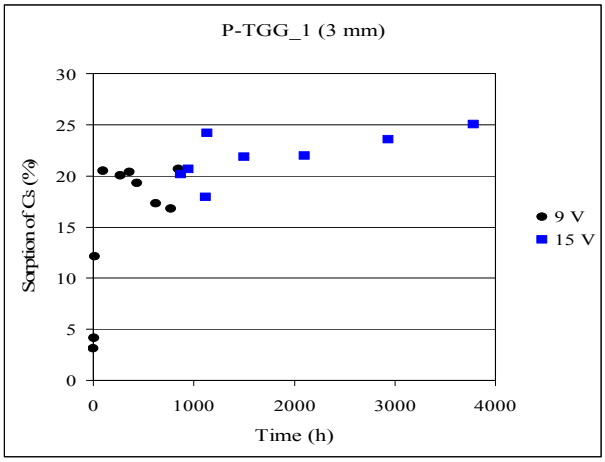

Figure 3-5. *Sorption of Cs on P-TGG gneiss slice 1. The voltages used in the experiments are indicated.*

Accessibility of variable charge sorption sites in intact rocks

It has been demonstrated that in intact rocks also, transition elements, lanthanides and actinides are sorbed mainly to dark minerals (e.g. Pinnioja et al. 1985, Suksi et al. 1987, Kaukonen et al. 2000, Olin et al. 2006). Densities of hydrolysable sorption sites in different minerals are poorly known. For the nuclides that are sorbed by surface complexation, it is in this report roughly estimated that sorption on different minerals is in direct correlation to the surface area of the minerals. The high surface area minerals in the rocks are micaceous minerals, hornblende and clays. Our simplistic approach is that, in the intact rock, sorption by surface complexation takes place only on the micaceous minerals and hornblende.

No direct experimental results are available to show that in intact rock all of the surface area of micas (see *Surface area of rocks*) is accessible for sorption for nuclides that are sorbing by surface complexation. For crushed Olkiluoto mica gneiss and tonalite, the R_d values of Ni measured to the crushed rock could be reproduced by measuring sorption on the separated biotites also at the pH where the hydroxo complexes were the main Ni solution species (see Ni Chapter 11). Combining this result with the accessibility of the sorbing minerals to hydrolysable tracers in diffusion experiments and C-14-PMMA experiments and accessibility of cation exchange sorption sites to Cs, the authors do not see any reason why the accessibility of sorption sites in the micas for surface complexation should be lower than that for cation exchange.

Different from cation exchange, in surface complexation it is estimated that on crushed rocks all accessible mineral surfaces have the same sorption site density and sorption affinity. This simplification is used in the derivation of crushed rock to intact rock conversion factors.

Surface area of rocks

The preference of sorption by surface complexation to micaceous minerals and clay minerals in the rocks is based on the high surface area of these minerals compared with

the surface area of unaltered feldspars and quartz. The specific surface areas (SA) determined by the BET/N_2 method of biotites from the Olkiluoto rocks were 0.5 m^2/g to 1.3 m^2/g (Kyllönen et al. 2008, Olin et al. 2006). The mean value was 0.8 m^2/g which was adopted for further calculations in this report. The surface areas of other micas, chlorite or hornblende in the Olkiluoto rocks have not been determined. The proportions of other micas, muscovite and sericite in the reference rocks are low compared to that of biotite, except in the pegmatitic granite. Muscovite and sericite are often very finely grained. So as not to overestimate the accessible surface area in the rock, the authors assumed here that their specific surface area (SA) and that of hornblende are the same as that of biotite. The accessible surface areas of intact rocks (Table 3-2) are calculated values and are derived from the total proportion of biotite, muscovite, chlorite, hornblende and sericite (Table 3-3). For P-TGG rock it was assumed that 50 % of the CEC derived from biotite content is accessible. For solutes sorbing by surface complexation the authors assume that 50 % of the surface area of micas + hornblende is accessible to sorption

Particle size distributions determined (Labtium Oy, Kuopio Finland) by dry sieving were about the same for the crushed reference rocks. For example, the proportion of particles smaller than 63 μm were 9.3, 7.9, 7.0 and 8.1 % for T-MGN, P-TGG, T-TGG and PGR, respectively (Appendix 1). Specific surface areas for samples of the crushed reference rocks were determined using the MICROMERITICS FLOWSORB 2300 instrument at the Tampere University of Technology, Institute of Earth and Foundation Structures. Owing to the relatively low surface areas for the smaller than 2 mm particle size crushed rocks, a fairly large range of BET/N_2 surface areas was found, as indicated in Table 3-3. The much larger result for the surface area of T-MGN than for the other rocks was unexpected. The surface area for the mica gneiss used in many experiments by Kulmala et al. in 1996-1998 was therefore adopted to represent the surface area of all mica gneisses. The SA values used further in this report for the crushed reference rocks, 0.9 m^2/g for gneissic rocks and 0.8 m^2/g for the crushed pegmatitic granite, are indicated in bold in Table 3-3. The uncertainty in the surface areas is taken into account as an uncertainty in the conversion of sorption on the crushed rock to sorption in the intact rock.

The inner surface areas of crystalline rocks have rarely been experimentally determined. André et al. (2008b) determined BET/N_2 surface areas for intact drill core samples and obtained by extrapolation calculated inner surface areas for different size fractions of crushed granite (KLX 04 Oskarsham) of 0.021 m^2/g and 0.04 m^2/g. Sample-specific mineral compositions are not given in Andre et al. (2008b). The modal biotite content of fresh granite in granites in deep drillings at Laxemar area was between 1.2 – 12 %. The calculated SA value (0.04 m^2/g) for the total micas + hornblende content (5.3 %) of the Olkiluoto pegmatitic granite PGR is in fair agreement with the BET/N_2 surface area value for the KLX 04 granite.

Table 3-2. *CEC values and calculated surface areas (SA) of intact rocks (T-MGN, T-TGG, P-TGG and PGR).*

Rock	Biotite (%)	SUM (%)	CEC (ueq/g)	SA (m^2/g)
T-MGN	21.2	26.3	3.18	0.21
T-TGG	8.2	11.5	1.23	0.092
P-TGG	22.0	25.0	1.69	0.10
PGR	0.9	5.3	0.135	0.042
SUM = biotite+chlorite+muscovite+sericite+hornblende (%) CEC = 15 µeq/g * proportion of biotite SA = accessible surface: T-MGN, T-TGG and PGR (0.8 m^2/g * SUM/100); P-TGG (0.5*0.8 m^2/g * SUM/100)				

Table 3-3. *Experimental surface areas of the crushed reference rocks and crushed Olkiluoto mica gneiss, tonalite (granodiorite) and granite and calculated surface areas (SA) for intact rocks. The SA values used further in this report are marked in bold.*

Rock	BET/N_2 (m^2/g)	Biotite (%)	Micas+hornblende (%)	SA** (m^2/g)
Ol1 MGN *	0.95	32.4	34.6	0.26
O2A TON *	0.22	6.6	16.6	0.18
Ol2B GR *	0.36	0.2	9.6	0.08
T-MGN	2.0	21.2±8	26.3	0.21
T-MGN	2.36 - 2.44 (**0.9**)	21.2±8	26.3	0.21
PGR	0.7- **0.8**	0.9±1.7	5.3	0.007 - 0.042
P-TGG	0.2 - **0.9**	22±7	25.0	0.10
T-TGG	0.26 - 1.6 (**0.9**)	8.2±7.5	11.5	0.09
Kulmala et al. 1996.* * surface area calculated from content of micaceous minerals and hornblende in the rocks (BET/N_2 0.8 m^2/g). To P-TGG the 50 % accessibility is used .*				

Surface area ratio as the R_d to K_d conversion factor

The R_d values for crushed rocks in the specific solution conditions were converted to the K_d value of intact rock by the ratio of calculated surface area of micas+hornblende (= SA for intact rock) to the measured (BET/N_2) surface area of crushed rock (Table 3-4).

An R_d value determined for rock material other than the reference rock is converted to a R_d for the reference rock in the experimental water by multiplying the source data R_d by the ratio of the micaceous minerals+hornblende in the rocks and further to K_d of the reference rock, using the conversion factors for the reference rocks (Table 3-5). In this conversion it is assumed that in crushed rock sorption also takes place mainly on micaceous minerals and hornblende, as suggested by the fact that sorption of Ni on crushed rocks was the same as on the amount of biotite in the crushed rocks (see Figures Ni-7a-7b and Ni-8a-8b in Chapter 11). This follows the fact that the R_d values (and further K_d values) derived from R_d value to a rock of higher mica+hornblende content than the reference rock may be low, and R_d values derived from data for rock of lower mica+hornblende than in the reference rock may be high. In this report, this concerns K_d values for I, Cl, Pu(IV), Pu (V,VI) and Np(V).

CEC ratio as the conversion factor

Following from the evaluation of CEC (Table 3-2) for the rocks, the sorption by cation exchange in a rock is taken to be solely on biotite and the K_d value for a rock is the same as the R_d value for crushed rock to which the accessible CEC of biotite is estimated to be 15 µeq/g (0.8 m^2/g) to T-MGN, T-TGG and PGR and 7.5 µeq/g (0.4 m^2/g) for P-TGG. For rock to rock conversion of R_d values, the ratio of amounts of biotites was used as the conversion factor.

In some cases (Ag, Be) there is no site- or material-specific data of sorption of a nuclide on the rocks. In these cases, backup for the selection of K_d values is derived from the data of the sorption measurements in well-defined experimental conditions. In these cases the available data on CEC or surface area is used for derivation of values for the Olkiluoto rocks in the experimental waters. Sorption of beryllium on the rocks was derived from sorption on illite using the CEC values of illite and rock as the conversion factor.

Derivation of K_d values of Cs for intact rocks was made using a using cation exchange model (Chapter 7) and for alkaline earth cations (Chapter 10), assuming that sorption to crushed rocks was mainly (90 %) on biotite.

Table 3-4. *Derivation of K_d values for intact rocks from R_d values for crushed rocks. SUM MICAS = proportion of biotite+chlorite+muscovite+sericite+hornblende in the rocks (Kärki & Paulamäki 2006) BET/N_2 = surface area of crushed rock, SA= calculated accessible inner surface area for intact rock, K_d = mean value for mass distribution.*

Rock	SUM MICAS (%)	BET/N_2 (m^2/g) Crushed rock	SA (m^2/g) (0.8*SUM MICAS*accessibility)*	R_d to K_d Conversion factor	K_d **
T-MGN	26.3	0.9	0.21	0.23	R_d*0.23
P-TGG	25.0	0.9	0.10*	0.11[1]	R_d*0.11
T-TGG	11.5	0.9	0.09	0.10	R_d*0.10
PGR	5.3	0.8	0.042	0.05	R_d*0.05

*Accessibility of sorption sites in P-TGG is 50 %; **K_d for intact rock in experimental water.

Table 3-5. *Derivation of K_d values for intact reference rocks from R_d values for other crushed rocks used in in-house experiments. SUM = biotite+chlorite+muscovite+ sericite+hornblende (%) in the rocks. Exp = value in source data, BET/N_2 = surface area of crushed reference rock, SA= calculated inner surface area for intact reference rock, K_d Ref = mean value for mass distribution in the source data water.*

Rock	SUM MICAS (%) Exp	SUM MICAS (%) Ref	R_d Exp	MICAS Ref/Exp	R_d Ref	R_d to K_d (Scaling Factor)	K_d* Ref
T-MGN	A	26.3	B	26.3/A	(26.3/A)*B	0.23	R_d*0.23
P-TGG	A	25.0	B	25.0/A	(25.0/A)*B	0.11	R_d*0.11
T-TGG	A	11.5	B	11.5/A	(11.5/A*B)	0.10	R_d*0.10
PGR	A	5.3	B	5.3/A	(5.3/A*B)	0.05	R_d*0.05

*K_d for intact reference rock in the source data experimental water.

3.3.2 Clays and Argillaceous rocks

Clays are composed of finely divided mineral particles. Van Loon et al. (2009) showed that the same amount of cation exchange sorption sites was accessible to cesium in dispersed and intact Opalinus clay rock. This suggests that the R_d values determined for dispersed clays are applicable to be used as K_d values for intact clays. It is generally assumed that in the clays and clay rocks the same amount of sorption sites as in dispersed clay is accessible to sorption, as in the following examples.

Bradbury & Baeyens (2011) calculated sorption on Opalinus argillite by using their sorption database of sorption on dispersed illite in electrolyte solution. No scaling from dispersed to intact clay was made, as suggested by the accessibility of Cs sorption sites in the clay (Van Loon et al. 2009). Only the illite-smectite clay in the rock was assumed to be an important sorbent. Good agreement with the modelled and experimental sorption was found.

Bradbury & Baeyens (1998, 2003) and Bradbury et al. (2010) estimated sorption transfer factors for Opalinus clay rock formation. Sorption data to non-Opalinus illite in the literature was also used. The ratio of cation exchange capacity of suspended Opalinus clay illite to the CEC value of illite in the referred publication was used to derive K_d values for Opalinus illite. The speciation of the solute was used to estimate the effects of differences in the composition of the waters on the sorption.

Sorption K_d-values for Th, Np, Cs, and Se valid for Honorobe argillaceous rocks in Japan were derived by Ochs et al. (2008) using the JNC SDB sorption database. The clay was assumed to be the dominant sorbing mineral. Modelling was applied only to the speciation of the nuclides in the solutions. Scaling for mineralogical properties was based on CEC values for the minerals or BET/N_2 surface area. The scaling factor from dispersed rock to intact rock was 1.

Implication for accessibility of sorption sites in the fracture coating clays in Olkiluoto

The fracture coating clay layers in Olkiluoto are thin. The thickness of the coatings is mostly less than 2 mm (Gehör et al. 2007a, b, c, d, e, f). Sporadically thicker clay layers of hydrothermal origin were found (Gehör 2007). The conversion factor used between a R_d value for dispersed clay in the sorption experiments to intact surface-coating clay K_d value was 1.

3.4 Estimation of uncertainty in K_d values for rocks

Conversion of R_d values in the source data to K_d values in the target conditions includes estimation of mineralogical properties and solution chemistry of source data and target conditions and the uncertainties in conversion. The total uncertainty is composed of the accuracy of source sorption data and uncertainties in mineralogical and solution chemical parameters and the thermodynamic database (TDB) used for speciation and for calculation of sorption. Uncertainties are estimated as uncertainty factors.

Uncertainties in rock and mineral material properties of rocks

Different cases and sources of uncertainty (italics) in solid material properties affecting conversion of R_d values to K_d values for the reference rocks.

1. Calculation of K_d for Cs

    Proportion of biotite in rock
    CEC of biotite

2. Conversion of R_d data for the reference rocks to K_d for intact rocks

    Proportion of micaceous minerals+hornblende in the rocks
    SA of crushed rocks
    SA of micaceous minerals+hornblende

3. Conversion of R_d data of other Olkiluoto rocks to K_d of reference rocks

    Proportion of micaceous minerals+hornblende in the rocks
    SA of crushed rock
    SA of micaceous minerals+hornblende

4. Conversion of R_d data of Ag and Be to clays to K_d of reference rocks

    Proportion of biotite in the rock
    SA of crushed rock
    SA of micaceous minerals+hornblende
    CEC of biotite
    CEC of clay

3.4.1 Uncertainties in characterisation of the properties used for conversions

The relative errors in the mineral properties are given as uncertainty factors for estimations of total uncertainty of K_d values.

Proportions of biotite and micas in the rocks

Proportions of the minerals and standard deviations of the proportions in the reference rocks are given in Appendix 1 (Kärki & Paulamäki 2006). The mean of the proportions of micaceous minerals+hornblende, the maximum error and standard deviation for gneisses T-MGN, P-TGG, T-TGG and PGR granite are shown in Table 3-6.

Values for P-series (P-MIGGN) and T-series (T-MIGGN) migmatic gneisses in Olkiluoto (Kärki & Paulamäki 2006) are also given to complement the data on minerals in the Olkiluoto rocks. The values in bold (1.4) are used for T-MGN and P-TGG. For other Olkiluoto rocks used in the in-house experiments, only the mean mineral compositions are known. The uncertainty factor 2.3 is used for other Olkiluoto gneissic rocks, as the uncertainty coefficient of proportion of micaceous minerals+hornblende.

Table 3-6. *Mean values (MEAN, %), maximum errors (ERRmax, %), standard deviations (MAXstd, MINstd, %) of sum of micaceous minerals+hornblende in the reference rocks and uncertainty factors (UFmax, UFmin) based on mean, maximum and minimum proportions of the minerals. Values to P-series (P-MIGGN) and T-series (T-MIGGN) migmatic gneisses are also given.*

Rock	MEAN	ERRmax	ERRstd	MAXstd	MINstd	UFmax/mean	UFmean/min
T-MGN	26.1	14.7	9.92	36.0	16.2	**1.4**	1.6
P-TGG	24.5	10.8	7.40	31.9	17.1	1.3	**1.4**
T-TGG	11.5	12.5	8.13	19.6	3.37	-	-
PGR	5.3	8.3	4.47	9.8	0.83	-	-
P-MIGGN	27.1	19.5	10.6	37.7	16.5	1.4	1.6
T-MIGGN	33.9	42.6	19.2	53.1	14.7	1.6	**2.3**

Table 3-7. *Mean values (MEAN, %),standard deviations (MAXstd, MINstd, %) of biotite in the reference rocks and uncertainty factors (UFmax, UFmin) based on mean, maximum and minimum proportions of the minerals. Values to P-series (P-MIGGN) and T-series (T-MIGGN) migmatic gneisses are also given.*

Rock	biotite	Std_dev	MAXstd	MINstd	UFmax/mean	UFmean/min
T-MGN	21.2	8.4	29.6	12.8	1.4	1.7
P-TGG	22.5	7.1	29.6	15.4	1.3	1.5
T-TGG	8.2	7.5	15.7	0.7	1.9	11.7
PGR	0.9	1.7	2.6	-0.8	-	-
T-MIGGN	22.7	9.9	32.6	12.8	1.4	1.8
P-MIGGN	20.2	14.3	34.5	5.9	1.7	3.4

Uncertainty factors of proportions of biotite were derived as for the sum of micaceous minerals+hornblende. The UF factors (Table 3-7) for T-MGN and P-TGG are a little higher than for the sum of micaceous mineral+hornblende (Table 3-6).

For the T-MGN and P-TGG, an uncertainty factor (UF) value of 1.4 is proposed for the sum of micaceous minerals and hornblende. In T-TGG gneiss and PGR granite the heterogeneity of the mineral composition was high and the maximum error was larger than the mean proportion of micaceous minerals. In PGR the proportion of biotite was very low, 0.9 ± 1.7 %, and most of the micaceous minerals were muscovite and sericite. For this reason, only total uncertainty factors are proposed for T-TGG and PGR.

BET/N_2 surface area of crushed rocks

Uncertainty coefficient = 2

BET/N_2 surface area determinations for < 2 mm crushed Olkiluoto rocks were made for sorption experiments in works reported during 1995–1998 (e.g. Pinnioja et al. 1984, Suksi et al. 1987, Huitti et al. 1996, Kulmala et al. 1996) and for the reference rocks used in the experiments reported in this report. Results for the Olkiluoto rocks are given in Table 3-3. As the best estimate for crushed gneissic rocks, the value 0.9 m^2/g to T-MGN, P-TGG and T-TGG and 0.8 m^2/g to pegmatite granite PGR were selected, respectively. These values are used for conversion of sorption of crushed rock to K_d for

intact rocks. The uncertainty factor was calculated as the ratio of the high (2 m^2/g) measured value of mica gneiss to the best estimate value of 0.9 m^2/g.

BET/N_2 surface area of biotite

Uncertainty coefficient = 1.6

The BET/N_2 for the surface area of Olkiluoto biotites (0.25–1 mm) was 0.5–1.3 m^2/g. The mean SA value for biotite that was separated from Olkiluoto mica gneiss and granodiorite was 0.8 m^2/g. The micaceous minerals taken into account consist of biotite, muscovite and sericite. The surface area (m^2/g) of especially often fine-grained sericite may be much higher than that of biotite and muscovite. A value of 0.8 m^2/g is used as the best estimate in this work. The same value is also used for hornblende. The uncertainty coefficient is the ratio of the upper value for surface area 1.3 m^2/g to the best estimate and has a value of 1.6.

Cation exchange capacity of biotite

Uncertainty coefficient = 2

CEC values of biotites that were separated from Olkiluoto mica gneiss and granodiorite were determined for Na, K, Ca and Mg cations in Kyllönen et al. (2008) and Olin et al. (2006). The value used in calculation of sorption of Cs on the rocks is the median value. The precision of the determinations was about 20 %. It is however taken that an error of 50 % covers all types of biotite in the reference rocks.

3.4.2 Combination of errors in characterisation of the properties used for conversions

Uncertainty factors owing to errors in rock/mineral data for the calculation of lower limit K_d values from the best estimate K_d values are given below. It is here assumed that the error in biotite and mica surface area is included in errors of surface area of the crushed rock. The lower limit K_d value is the best estimate K_d divided by the uncertainty factor.

1. K_d for the reference rocks from R_d for the reference rocks

	mica	biotite
T-MGN, P-TGG	5	7
T-TGG	20*	
PGR	50*	

2. K_d for the reference rocks from R_d data to other Olkiluoto rocks

	mica	biotite
T-MGN, P-TGG	15	18
T-TGG	20*	
PGR	50*	

3. K_d values for reference rocks from in-house sorption data to biotite

	mica	biotite
T-MGN, P-TGG	7	8
T-TGG	20*	
PGR	50*	

4. Literature data for well-defined silicate/clay minerals in relevant ionic strength solution to K_d for the reference rocks using CEC or BET surface area values. Errors are case dependent.

* error propagation using the errors in only biotite contents and BET/N_2 surface area of crushed rock yield unrealistically low correction factors for T-TGG and PGR. To give more weight to biotite as the sorbing mineral, and because the correction factors for biotite are more conservative, they are used for all elements but Cs. The values marked with an asterisk are estimated to be reasonably low. For T-MGN and P-TGG the mean correction factor for these rocks is used.

3.4.3 Uncertainties owing to source data and solution chemistry

Uncertainties in source data are case-specific and are evaluated per case. Uncertainties due to solution conditions are element specific and are evaluated for the water conditions.

3.4.4 Total uncertainty

The total uncertainty factor is calculated as the product of the uncertainty factors. The lower limit K_d values are given as K_d/UF_{tot} This approach is generally adopted for clays and clay rocks (Bradbury & Baeyens 2003, Ochs et al. 2008).

3.5 Estimation of uncertainty in K_d values for clays

3.5.1 Mineralogy

Kaolinite

KGa-1b, a well-crystallised kaolinite from the U.S. Clay Minerals Society, was used in the in-house experiments. This clay was also used in most of the sorption studies on kaolinite referred to in this report. As the CEC of kaolinites is much lower than that of trioctahedral clays (illite, smectites) the BET/N_2 surface area is regarded as the best measure of sorption site concentration. The BET/N_2 value for the KGa-1b 10-12 m^2/g is at the low end of the values given to kaolinites in the referred sorption studies. The BET/N_2 surface area of less crystallised kaolinites is also larger and accompanied by higher CEC (negative internal charge). The kaolinite in Olkiluoto is not well known. It is here assumed that sorption area of Olkiluoto kaolinite is the same as (not higher than) that of KGa-1b. When the BET/N_2 surface area of a kaolinite, different from that of KGa-1b, is given in the source data, the sorption is converted to the surface area of KGa-1b. The conversion factor is the ratio of surface areas. Only the best estimate and lower limit K_d values are given in this report and it was regarded as sufficient to use the UF factor (1) for uncertainty in the surface area of the kaolinite.

Illite

IMt-1 (Silver Hill) illite from the U.S. Clay Minerals Society was used in the in-house sorption studies. The proportion of swelling clay minerals that may increase the CEC is low in Silver Hill illite. The CEC of this illite is well within the range of CEC values for different illites, including the Opalinus clay or illite de Puy on which many of the referred sorption studies were made. The illite on Olkiluoto fracture surfaces is not well defined. It is assumed here that the sorption properties of Olkiluoto illite are the same as those of IMt-1 and illites in the referred studies. The CEC for the illites ranges from 170 meq/kg to 250 meq/kg. The CEC used in this report for calculation of Cs sorption is 225 meq/kg, as determined for Cs in Baeyens & Bradbury (2004). The UF_{cec} value of 1.3 is derived as 225/170.

Chlorite

The chlorite used in the in-house sorption experiments, ripidolite CCa-2 (Flagstaff Hill, El Dorado California), was from the U.S. Clay Minerals Society collections. For chlorite, K_d values are given only for the radionuclides to which sorption experiments were performed for this report. The properties of Olkiluoto chlorites are not known. The same uncertainty factors in sorption capacity as for illite and lab to field uncertainty factors are used.

3.5.2 Solution chemistry and source data

pH

Selection of the K_d values is based on in-house experimental values for the groundwater simulants and/or literature sorption data. Uncertainty in measurement of pH is estimated to 0.2 pH units. The uncertainty is case specific and depends on the pH-sensitivity of sorption. The impact on R_d depends on the pH dependency of sorption at relevant pH.

Speciation

The differences in speciation in source data and target conditions are evaluated and the fraction of sorbing species (FSS) is used to correct the K_d values. This approach is used only when sorption data and speciation of the radionuclide are not in agreement. The uncertainty in this conversion is due to uncertainties in the TDB. In this report, the authors have adopted the UF_{spec} value 1.4 proposed by Hummel & Berner (2002). This uncertainty factor is used in all cases when there are differences in speciation between source and reference conditions.

Chemical analogues

For some radionuclides, no relevant sorption data was available and sorption data was derived from a chemical analogue. In most cases, the chemical analogue nuclide was selected based on the hydrolysis properties of the nuclides. In the selection of K_d values, more weight was given to the experimental sorption behaviour of the analogue nuclides (e.g. Eu/Am/Pu(III)) than to differences in speciation of the source and target nuclide in solutions.

Source sorption data

The uncertainty factor UF_{source} of 1.6 for R_d values was derived from sorption edge measurements (Bradbury & Baeyens 2003). This value is typical of R_d values determined for illitic clays. For the in-house measurements, the uncertainty factor is estimated individually based on how the best estimate R_d values were selected.

Sorption model calculation

For UF_{model} to sorption data obtained for illite by model predictions (Cs, Sr, Ra), an uncertainty factor of 3 was used in Bradbury & Baeyens (2003). For sorption of Cs, Sr and Ra on kaolinite, the UF_{model} was estimated individually.

Lab to field transfer factors

The lab-to-field transfer factor, as the best estimate, was assumed to be unity as proposed by Bradbury & Baeyens (2003) based on the BET/N_2 surface area of crushed and intact clays and sorption and diffusion in clays and sorption of Cs on crushed and intact argillaceous rock (Van Loon et al. 2009). The accessibility of sorption sites in Olkiluoto kaolinite, illite and chlorite is assumed to be 50 % at lowest, and the UF_{lab_field} factor of 2 is used.

3.5.3 Total uncertainty

The total uncertainty factor is calculated as the product of the UF-factors. The lower limit K_d values are given as K_d/UF_{tot} This approach is generally adopted for clays and clay rocks (Bradbury & Baeyens 2003, Ochs et al. 2008).

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4 CARBON

Carbon exists in the Olkiluoto groundwaters at the oxidation state –IV, forming carbohydrates, especially methane and probably low molecular weight organic acids, and/or at the oxidation state +IV, forming carbonates. It is assumed (Pitkänen et al. 2007) that the concentration of DOC (dissolved organic carbon) in deep groundwaters at Olkiluoto is much lower than measured due to contamination from packers and uncertainties in the amounts of hydrocarbons in the analysed waters. The measured DOC concentrations are highest at the shallow depths. In the metamorphic rock types, small amounts of accessory graphite (C(0)) are common. It is assumed to be non-reactive. Next, we will focus on inorganic carbon.

4.1 Speciation

Inorganic carbon exists in groundwater environments as dissolved carbon dioxide (CO_2 (aq)), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, the proportions of which depend on the pH of water. In the pH region of interest in the bedrock, the main species is bicarbonate. In granitic groundwaters, the total carbonate concentration varies from very low values in methanic waters to $2 \cdot 10^{-3}$ M in surficial groundwaters. The carbonate concentration in the non-methanic waters is often determined by saturation with respect to calcite. Carbonate ions form soluble complexes, especially with di- and multivalent cations, oxycations like uranyl and neptunyl ions and form a part of the ternary complexes of lanthanides and actinides.

4.2 Sorption on rocks

The negatively charged bicarbonate and carbonate ions are only weakly or not at all sorbed on silicate minerals but more probably on iron oxides in analogy with sulphate (SO_4^{2-}) (Dzombak & Morel 1990). Sorption of carbonate to ferric oxides is modelled to be mainly by bidentate inner sphere complexation of carbonate, and in a closed system has a sorption maximum at around pH 6 (Villalobos & Leckie 2001, Rahnemaie et al. 2007). Outer sphere complexation of carbonate to positively charged surface sites in, for example, goethite is much less important. Sorption at pH higher than 8.5 is also very low on iron oxides. The decrease of solution concentration of carbonate is more probably due to precipitation as calcite or isotopic exchange to existing calcite (Allard et al. 1981, Allard 1985).

Allard et al. (1981) and Andersson et al. (1982) have measured the R_d values of $1 \cdot 10^{-3}$ m^3/kg for the sorption of carbonate on calcium-containing minerals, $2.2 \cdot 10^{-3}$ m^3/kg for sorption on clayish till and $8.3 \cdot 10^{-2}$ m^3/kg for sorption on calcite.

4.2.1 Source data

Sorption R_d values on rock and concrete sand ballast in low-salinity Olkiluoto groundwater have been $(1\text{-}2) \cdot 10^{-3}$ m^3/kg (Hietanen & Alaluusua 1984, Pinnioja et al. 1984). No sorption on Stripa granite was found ($R_d = 0$) (McKinley & Haderman 1984). Baik et al. (2010) give K_d values of $(5\text{-}6) \cdot 10^{-3}$ and $(1.0\text{-}1.2) \cdot 10^{-2}$ m^3/kg at pH 6.5 to 7.5

in low-salinity groundwaters for Korean crushed granodiorite and fracture-filling, respectively.

R_a values for sorption on thin sections were lower than the determination limit ($1 \cdot 10^{-4}$ m^3/m^2). In rock pieces exposed to C-14-carbonate solution, the dark minerals indicated the presence of attached carbonate. This may be due to the penetration of carbonate to pores in these minerals or sorption on trace iron oxides that are common in biotite.

In higher pH groundwaters and in cement modified groundwaters, the retardation of C-14 is controlled by calcite, either by sorption or by isotopic exchange. Owing to uncertainties in the formation of calcite, the sorption of C-14 in cement modified conditions is taken to be very low.

No new in-house data in reference water conditions and for reference rocks are available. The earlier in-house data are scarce, therefore other above mentioned source data are also considered.

4.2.2 Best estimate K_d values

Owing to difficulties in the determination of sorption of carbonate on rock material in groundwater and in order not to overestimate sorption, carbonate is suggested to have very low K_d values of inorganic carbon, therefore no specific best estimate K_d value is given.

4.2.3 Lower limit K_d values

Owing to the above mentioned difficulties, no specific lower limit K_d value is given.

4.3 Sorption on clays

4.3.1 Source data

No in-house data or open source information in reference water conditions and for reference clays are available.

4.3.2 Best estimate K_d values

Owing to a lack of sufficient relevant information, no specific best estimate or lower limit K_d value is given.

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5 CHLORINE

5.1 Speciation

Chlorine occurs in the form of chloride ion (Cl^-) in groundwater environments. Chloride is one of the main anions in the Olkiluoto groundwaters. In the reference waters the chloride concentration varied from $1 \cdot 10^{-4}$ M in the glacial meltwater OLGA to 0.4 M in the saline groundwater OLSR. Chloride is highly soluble in groundwater conditions.

5.2 Sorption on rocks

5.2.1 Source data

Sorption in groundwater conditions

Sorption of chloride on crushed Olkiluoto granodiorite and mica gneiss and on rapakivi granite in ALLARD water and in brackish natural groundwater has been reviewed in Kulmala & Hakanen (1992). The R_d values for crushed rocks were from $3 \cdot 10^{-4}$ m^3/kg to $1 \cdot 10^{-3}$ m^3/kg. In the reviewed experiments, sorption was determined from decreases of the tracer Cl-36 activities in solutions and include errors due to only small differences in Cl^- concentration in standard solution and analyte. The results anyway indicate that sorption of chloride on crushed rocks is not zero in fresh and brackish waters. The sorption data for chloride on rocks are poor as compared to data for iodide. Iodide was used as a chemical analogue to chloride and K_d values of chloride were derived from values of iodide.

The K_d values of chloride ion for rocks is suggested to have values 1/3 of those for iodine in the conditions of this study (see Chapter 6 IODINE).

5.2.2 Best estimate K_d values

Tables Cl-1, Cl-2, Cl-3 and Cl-4 present the best estimate K_d values of chloride in the reference waters.

Table Cl-1. *The best estimate K_d (m^3/kg) values of chloride for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E-04**	**2.0E-04**	**6.7E-06**	**1.7E-06**	**1.3E-07**	**1.0E-05**	**1.0E-06**
10	2.0E-06	2.0E-06	2.0E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-2. *The best estimate K_d (m^3/kg) values of chloride for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E-04**	**1.0E-04**	**3.3E-06**	**8.3E-07**	**6.7E-08**	**5.0E-06**	**5.0E-07**
10	1.0E-06	1.0E-06	1.0E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-3. *The best estimate K_d (m^3/kg) values of chloride for T series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.7E-05**	**6.7E-05**	**1.7E-06**	**3.3E-07**	**2.0E-08**	**3.0E-06**	**5.0E-08**
10	3.3E-07	3.3E-07	3.3E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-4. *The best estimate K_d (m^3/kg) values of chloride for pegmatite granite PGR at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.3E-05**	**1.3E-05**	**3.3E-07**	**1.0E-07**	**6.7E-09**	**6.7E-07**	**6.7E-08**
10	9.0E-08	9.0E-08	9.0E-08	0.0E+00	0.0E+00	0.0E+00	0.0E+00

5.2.3 Lower limit K_d values

The lower limit K_d values of chloride in the reference waters are calculated by dividing the best estimate K_d values by the uncertainty factor. The lower limit K_d values are presented in Tables Cl-6 to Cl-9.

Table Cl-5. *Factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	7
P-TGG	7
T-TGG	20
PGR	50

Table Cl-6. *The lower limit K_d (m^3/kg) values of chloride for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.9E-05**	**2.9E-05**	**9.5E-07**	**2.4E-07**	**1.9E-08**	**1.4E-06**	**1.4E-07**
10	2.9E-07	2.9E-07	2.9E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-7. *The lower limit K_d (m^3/kg) values of chloride for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.4E-05**	**1.4E-05**	**4.8E-07**	**1.2E-07**	**9.5E-09**	**7.1E-07**	**7.1E-08**
10	1.4E-07	1.4E-07	1.4E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-8. *The lower limit K_d (m^3/kg) values of chloride for T series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.3E-06**	**3.3E-06**	**8.3E-08**	**1.7E-08**	**1.0E-09**	**1.5E-07**	**2.5E-09**
10	1.7E-08	1.7E-08	1.7E-08	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-9. *The lower limit K_d (m^3/kg values of chloride for pegmatite granite PGR at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.. KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E-07**	**2.7E-07**	**6.7E-09**	**2.0E-09**	**1.3E-10**	**1.3E-08**	**1.3E-09**
10	1.8E-09	1.8E-09	1.8E-09	0.0E+00	0.0E+00	0.0E+00	0.0E+00

5.3 Sorption on clays

5.3.1 Source data

Kaolinite

Sorption of anionic iodide on rocks was shown to have a good correlation with concentration of $AlOH_2^+$ sites on biotite surface at pH higher than the point of zero charge (PNZ) (see IODINE Figure I-1). Similar sorption behaviour is expected to chloride ions.

Bolland et al. (1976) determined both positive and negative charges on kaolinite using the exchange technique. The positive charge (Table 10) was determined by desorption of sorbed Cl^- and NO_3^- from the kaolinite after the NaCl, $NaNO_3$, CsCl or $CsNO_3$ solution equilibration of the kaolinites. The positive charge was higher at lower pH but was measurable up to pH 9–10, especially after equilibration in high ionic strength solutions. R_d values of chloride ions in Table Cl-10 were derived from Figures 1b and 2b in Bolland et al. (1976). The decrease of R_d values of Cl^- from pH 6 to pH 8 is about the same, a factor of 2.5 – 3.2 in the $1 \cdot 10^{-3}$ M and $1 \cdot 10^{-2}$ M CsCl solutions.

For the halogenide anions, the sorption affinity on kaolinite is $I^- > Br^- > Cl^-$ (Weerasooriya 1999). No other dependences of solution ion composition on sorption of chloride to kaolinite have come to the attention of the authors.

Illite

Sorption of chloride ions is estimated to be very low on illite and montmorillonite in brackish Opalinus clay water (Bradbury and Baeyens 2003a, 2003b). K_d values of chloride for illite were derived from K_d values of iodide on Opalinus clay in OPA pore water ($3 \cdot 10^{-5}$ m^3/kg and $4 \cdot 10^{-5}$ m^3/kg) (Bradbury and Baeyens 2003a).

Table Cl-10. *Sorption of chloride on API-9 (American Petroleum Institute) and U.S .Clay kaolinites (calculated from Bolland et al. 1976). The surface area (BET/N_2)and the positive charge of kaolinite are indicated in the table.*

kaolinite	BET m^2/g	pH	solution M	positive charge cmmol/100 g	R_d m^3/kg
API-9	20	6	CsCl 1E-3	0.3	3.50E-03
		8	CsCl 1E-3	0.1	1.10E-03
API-9	20	6	CsCl 1E-2	0.5	5.00E-04
		8	CsCl 1E-2	0.2	2.00E-04
U.S.Clay	13	6	NaCl 1E-3	0.1	1.10E-03

5.3.2 Best estimate K_d values

Kaolinite

The R_d value for API-9 kaolinite in 0.01 M CsCl solution at pH 8 (Table Cl-10) was taken as the base value. The R_d value of the API-9 kaolinite was converted to KGa-1b kaolinite by dividing the value of API-9 by two, the ratio of BET/N_2 surface areas of the kaolinites. Starting from this value, the K_d values in the other waters were calculated using the ratios of the K_d values of chloride (iodide) to T-MGN rock.

Illite

The K_d values of chloride for illite were calculated from K_d values for Opalinus clay in OPA pore water. For rocks, the K_d values of chloride were estimated to be one third of K_d values of iodide. The salinity and pH of brackish water OLBA is the nearest to OPA

pore water and K_d of chloride for illite in OLBA is taken to be one third of K_d of iodide on Opalinus clay. The K_d values of chloride in the other waters have the same ratios as sorption on T-MGN rock.

The best estimate K_d values of chloride for kaolinite and illite are given in Tables Cl-11 and Cl-12.

Table Cl-11. *The best estimate K_d (m^3/kg) values of chloride for kaolinite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-03**	**3.0E-03**	**1.0E-04**	**2.5E-05**	**2.0E-06**	**1.5E-04**	**1.5E-05**
10	3.3E-05	3.3E-05	3.3E-05	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table Cl-12. *The best estimate K_d (m^3/kg) values of chloride for illite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.2E-03**	**1.2E-03**	**4.0E-05**	**1.0E-05**	**8.0E-07**	**6.0E-05**	**6.0E-06**
10	1.3E-05	1.3E-05	1.3E-05	0.0E+00	0.0E+00	0.0E+00	0.0E+00

5.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{extrapol} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(Cl-1)}$$

The lower limit of value K_d(LL) is obtained by dividing each best estimate value K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Cl-2)}$$

Kaolinite

UF_{tot} = 15 (1.5 * 5 * 1 * 1 * 1 * 2) the total uncertainty factor.

UF_{source} = 1.5. The uncertainty factor of the source data describes the uncertainty of the R_d values of the literature, from which the best estimate K_d values for kaolinite were calculated. The value of 1.5 covers the uncertainty in reading the graphs.

$UF_{extrapol}$ = 5. Extrapolation is made over large ionic strength and pH range. Between pH 6 and pH 8 the source data suggests a smaller decrease with increase of pH than used in the extrapolation, suggesting that we are not overestimating sorption.

UF_{CEC} = 1. Cation exchange capacity was not relevant here. The R_d values for API-9 kaolinite were downscaled to KGa-1b kaolinite using the BET/N_2 area ratio as the factor.

UF_{spec} = 1. The uncertainty of speciation factor is 1, because only one solution species exists in the reference waters.

UF_{pH} = 1. No corrections of K_d values with pH were made.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.
The lower limit K_d (m^3/kg) values of chlorine for kaolinite in the Olkiluoto geosphere are presented in Table Cl-13.

Table Cl-13. *The lower limit K_d (m^3/kg) values of chloride for kaolinite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E-04**	**2.0E-04**	**6.7E-06**	**1.7E-06**	**1.3E-07**	**1.0E-05**	**1.0E-06**
10	2.2E-06	2.2E-06	2.2E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Illite

UF_{tot} = 26 (5 * 2 * 1.3 * 1 * 1 * 2) the total uncertainty factor.

UF_{source} = 5. The uncertainty factor of the source data describes the uncertainty of the R_d values (iodine), from which the best estimate K_d values were derived. The value of 5 covers the uncertainty as proposed in Bradbury & Baeyens (2003).

$UF_{extrapol}$ = 2. Extrapolation is made over large ionic strength and pH range.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity. The cation exchange capacity (CEC) for pure illites is generally higher than that of OPA clay rocks. No conversion for differences of CEC values was made due to the fact that low CEC minerals may also have had an impact on sorption of iodide on the Opalinus clay. The uncertainty in the source material compared with the Olkiluoto site illite is taken into account in the uncertainty factor UF_{CEC} which was taken as 1.3.

UF_{spec} = 1. The uncertainty of speciation factor is 1, because only one solution species exists in the reference waters.

UF_{pH} = 1. No corrections of K_d values with pH were made.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of chloride for illite in the Olkiluoto geosphere are presented in Table Cl-14.

Table Cl-14. *The lower limit K_d (m^3/kg) values of chloride for illite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.6E-05**	**4.6E-05**	**1.5E-06**	**3.9E-07**	**3.9E-07**	**2.3E-06**	**2.3E-07**
10	5.0E-07	5.0E-07	5.0E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00

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6 IODINE

6.1 Speciation

Iodine is a redox-sensitive element. In the present groundwaters, iodide is in the form of the anionic iodide ion (I^-). In surface waters, part of the iodine may be in the form of iodate, IO_3^-. The proportion of IO_3^- of total iodine was calculated with the PHREEQC program using the Thermo_Chimie 7b database (ANDRA 2009). The proportion is at pH 8 for E_h +620 mV about 14 % but decreases to $1.5 \cdot 10^{-4}$ % at E_h +470 mV.

Iodide is highly soluble in groundwater because the metals forming sparingly soluble iodides (e.g. Pb, Ag) are present only in trace concentrations. In the Olkiluoto groundwaters the iodide concentration is $<10^{-7}$ to $1.4 \cdot 10^{-5}$ M (Hellä et al. 2014). The concentration increases with the depth and salinity of the groundwater.

6.2 Sorption on rocks

6.2.1 Source data

Pinnioja et al. (1986) give a range of $(0.7–1.0) \cdot 10^{-3}$ m^3/kg for sorption in Allard water on mica gneiss and tonalite. Sorption on rapakivi in low-salinity water was about the same as on Olkiluoto rocks at pH 6–8 but higher than on the other studied rocks at pH 5. This is probably because of the higher iron oxide content of rapakivi. In saline groundwater, the R_d values of iodide for rapakivi varied from $0.35 \cdot 10^{-3}$ m^3/kg to $0.64 \cdot 10^{-3}$ m^3/kg (Pinnioja et al. 1986).

Sorption of anions on ferric hydroxide takes place preferentially on positively charged iron oxides and decreases with increasing pH (Dzombak and Morel, 1990). The same pH dependency of sorption was also demonstrated for iodide in fresh Allard water on crushed Olkiluoto mica gneiss (GN), tonalite (TON) and granite (GR), Kivetty granodiorite and porphyritic granite, Romuvaara tonalite, mica gneiss and granite and Hästholmen rapakivi in the report of Kulmala et al. (1998). This report is the main reference for the derivation of K_d values for the rocks. For the Olkiluoto rocks, the R_d was $(2–3) \cdot 10^{-3}$ m^3/kg at pH 6 and $(2–3) \cdot 10^{-4}$ m^3/kg at pH 8. At pH 9.5 the R_d values were $(1–2) \cdot 10^{-5}$ m^3/kg (Tables 1, 3 – 6, Kulmala et al. 1998a).

The decrease of sorption with increase of pH has the same slope as the decrease of Al-OH_2^+-sites of the biotite aluminol (Bio_wOH_2^+ Bio_sOH_2^+) surface sites calculated using hydrolysis constants and site density values for biotite in Wang et al. (2001) (Figure I-1).

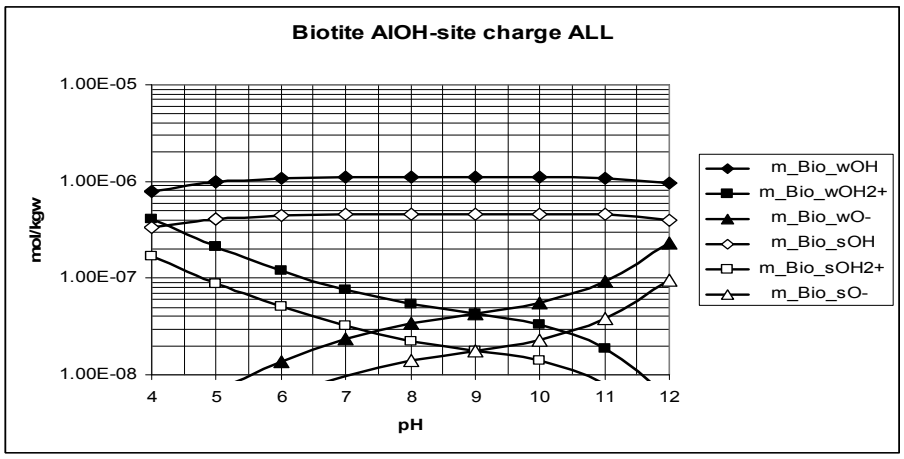

Figure I-1. *Calculated Al-OH site charges in biotite in ALLMR water for 1/10 solid to solution ratio for a rock containing 20 % biotite (DDL model, site density and pK values from Wang (2001), no interaction with electrolyte ions).*

Fuhrmann et al. (1998) have shown that in deionised water many common impurities in silicate minerals sorb trace concentrations of iodide in aerobic conditions. Pyrite is one of the iodide sorbing minerals. Pyrite and pyrite containing illitic shale showed the highest sorption of iodide. Pyrite is a minor constituent in Olkiluoto gneissic rocks and a common mineral on the surface of fractures (Kärki & Paulamäki 2006). In this report it is taken that its influence on sorption of iodide under groundwater conditions is insignificant.

6.2.2 Best estimate K_d values

K_d values in fresh ALLMR reference water

The K_d values for the reference rocks in ALLMR water were calculated from R_d values of crushed mica gneiss, granodiorite and granite using the ratio of the sum of biotite+ other micas+ hornblende in the rocks in Kulmala et al. (1998) and in the reference rocks, and converting the R_d values to K_d values using the conversion factors in Chapter 3 (Table 3-4). The K_d values for the reference rocks are presented in Figures I-2 to I-5. Owing to very low measured sorption, especially at the higher pH, the relative range of the K_d values increase with pH, even to orders of magnitudes.

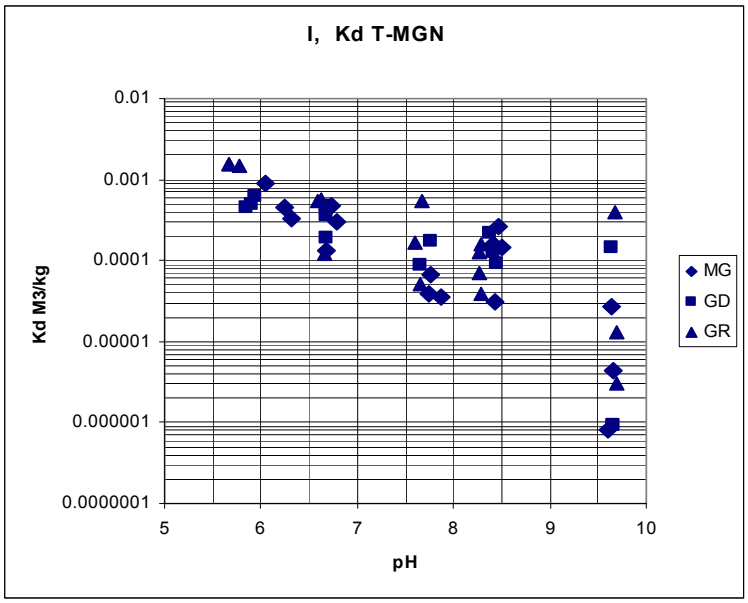

Figure I-2 *K_d values of I for T-MGN in fresh ALLMR water derived from values for MG, GD (TON) and GR Kulmala et al. (1998).*

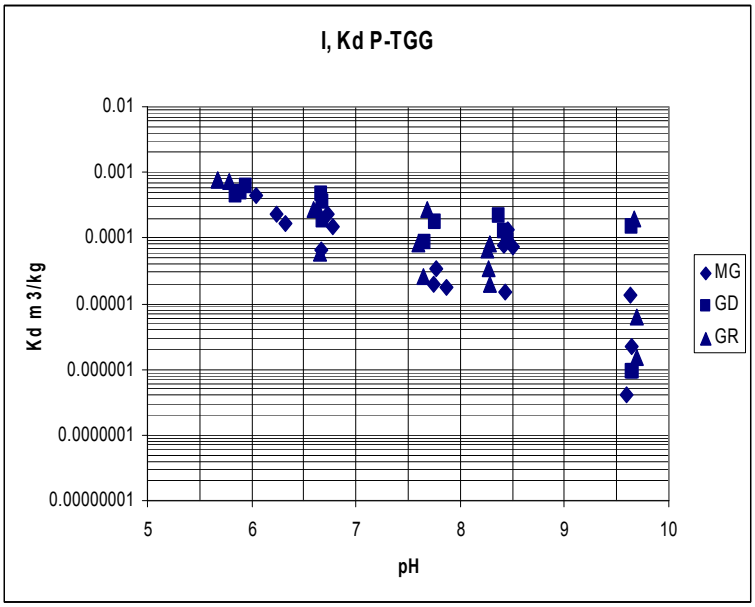

Figure I-3 *K_d values of I for P-MGN in fresh ALLMR water derived from values for MG, GD (TON) and GR Kulmala et al. (1998).*

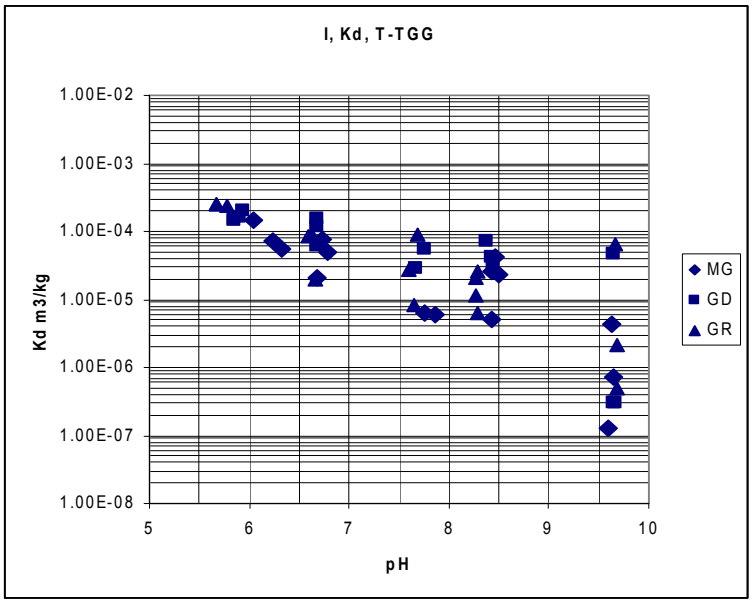

Figure I-4. *K_d values of I for T-TGG in ALLMR water derived from values for MG, GD (TON) and GR Kulmala et al. (1998).*

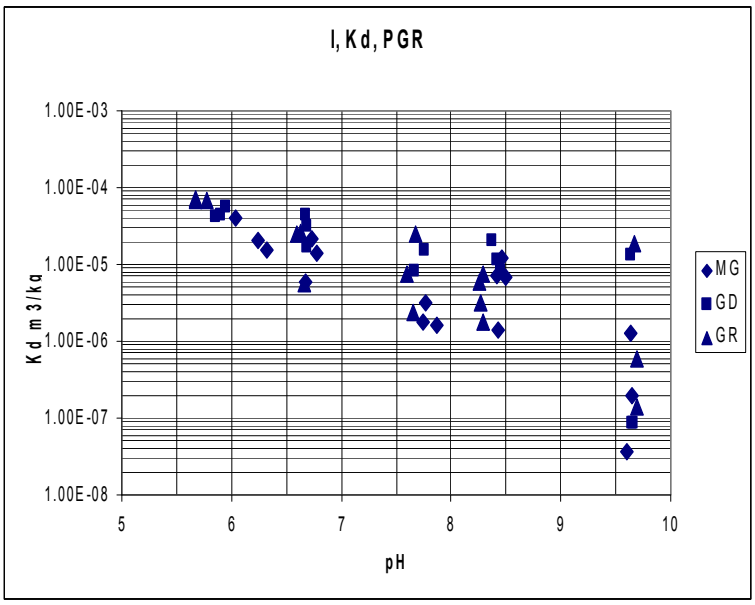

Figure I-5*. K_d values of I for PGR in ALLMR water derived from values for MG, TON and GR Kulmala et al. (1998).*

For the mica gneiss, the sorption was also measured by Kulmala using radioactivity counting of the crushed rock after removal of the solution. These measured relative sorption values are more accurately determined and indicate that the sorption in log-scale decreased linearly by two orders of magnitude between pH 5.5 and pH 9.5 (Figure 7 in Kulmala et al. 1998). The best estimate K_d values were chosen to have the same slope. The best estimate values in ALLMR water in aerobic conditions are given in Table I-1. The accessibility of sorption sites in P-TGG is also assumed to be 50 % for iodide.

Table I-1. *Best estimate K_d values (m^3/kg) of iodide in ALLMR water at pH 6 -10.*

pH	Rock			
	T-MGN	P-TGG	T-TGG	PGR
6	6.0E-04	3.0E-04	2.0E-04	4.0E-05
7	2.0E-04	1.0E-04	5.0E-05	1.0E-05
7.6	1.0E-04	5.0E-05	1.0E-05	6.0E-06
8	6.0E-05	3.0E-05	1.0E-05	3.0E-06
8.3	4.0E-05	2.0E-05	1.0E-05	2.0E-06
9	2.0E-05	1.0E-05	5.0E-06	1.0E-06
10	6.0E-06	3.0E-06	1.0E-06	3.0E-06

K_d values in groundwaters

K_d values for the reference rocks are derived from the values in ALLMR water at different pH and corrected for chloride concentrations in the reference waters.

K_d values in saline OLSR reference water

The measured R_d values for crushed mica gneiss in OLSO were low: in three out of four determinations the R_d value was lower than 0.01 mL/g at pH 7.5. In Kulmala et al. (1998a), the radioactivity count rate of iodine on the crushed rock (mean of four samples) was (4.3 ± 1.8) cpm/g. For mica gneiss in ALLMR water (pH 8.5) it was (95 ±65) cpm/g. Correcting this count rate to pH 7.5 gives the ratio of the count rates for ALLMR to OLSO water as (100 ± 80). This suggests that the K_d value of iodine in the OLSR water is lower than that in ALLMR by a factor of 100. The ratio of chloride concentrations in OLSO and ALLMR is 365. The K_d values of iodine in OLSR are suggested to be 100 times lower than in ALLMR at pH 8.3.

K_d values in saline KR20_465_1 groundwater

The ratio of Cl^- concentration in KR20_465_1 water to ALLMR is 116. It is assumed that the decrease of sorption by the higher salinity is relatively the same in OLSR. The K_d value of I in KR20_465_1 is estimated to be 3 % of that in ALLMR at pH 7.4.

K_d values in brackish OLBA reference water

The chloride concentration in brackish OLBA water is 70 times higher than in ALLMR. A rough estimation is here made that the K_d values of iodine in the OLBA water can be calculated from the K_d values in ALLMR by dividing the values for ALLMR by 20 (= 100/365* the ratio of chloride concentrations in the waters).

K_d values in brackish KR4_81_1 groundwater

The Cl-concentration in KR4_81_1 is 6.4 times that in ALLMR. The K_d values in KR4_81_1 are estimated to be 0.6 times those at pH 7.8 in ALLMR.

K_d values in glacial melt water OLGA

The chloride concentration of glacial OLGA water is 0.08 meq/L. This water also contains 0.004 meq/L of sulphate. The surface complexation constants of sulphate and selenate on ferric hydroxide are the same (Dzomback & Morel, 1990). This suggests that the sorption of the trace concentration of iodine may be lowered by competitive sorption of sulphate and other oxyanions. The total salinity of OLGA is lower than that of ALLMR and the ratio of Cl to sulphate is about the same as in ALLMR. The values derived in ALLMR at pH 6 do not overestimate sorption in OLGA, and the values in ALLMR are suggested for OLGA.

K_d values at pH 10

For the brackish and saline waters K_d value of 0 m^3/kg is suggested. For OLGA and ALLMR waters, the values at pH 10 in Table I-1 for ALLMR at pH are suggested.

Table I-2. *The best estimate K_d (m^3/kg) values of iodine for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-04**	**6.0E-04**	**2.0E-05**	**5.0E-06**	**4.0E-07**	**3.0E-05**	**3.0E-06**
10	6.0E-06	6.0E-06	6.0E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-3. *The best estimate K_d (m^3/kg) values of iodine for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-04**	**3.0E-04**	**1.0E-05**	**2.5E-06**	**2.0E-07**	**1.5E-05**	**1.5E-06**
10	3.0E-06	3.0E-06	3.0E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-4. *The best estimate K_d (m^3/kg) values of iodine for T series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E-04**	**2.0E-04**	**5.0E-06**	**1.0E-06**	**6.0E-08**	**9.0E-06**	**1.5E-07**
10	1.0E-06	1.0E-06	1.0E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-5. *The best estimate K_d (m^3/kg) values of iodine for pegmatic granite PGR at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.0E-05**	**4.0E-05**	**1.0E-06**	**3.0E-07**	**2.0E-08**	**2.0E-06**	**2.0E-07**
10	2.7E-07	2.7E-07	2.7E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00

6.2.3 Lower limit K_d values

Scattering of K_d values for the rocks in ALLMR water increases with pH (see Figures I-2 to I-5 and Tables I-3 to I-4). This is in part due to the scattering of the measured R_d values and in part due to conversion of R_d values for the rocks used in Kulmala et al. (1998) to K_d values for the reference rocks. The scattering of the K_d values in Figures I-2 – I-5 include the error from mineral heterogeneity of the source sorption data. The lowest values at pH 5.7 to pH 8.4 in the figures are within a factor of 2.5–3 with the best estimate values. Uncertainty in estimation of chloride concentration in the waters is highest in the saline waters due to the fact that the source data was mainly from fresh water conditions. At highest, this uncertainty is covered by a factor of 3. A total uncertainty factor of 7 is proposed for high-mica rocks, T-MGN and P-TGG. The mineralogical uncertainty of T-TGG and PGR rocks is much higher than the uncertainty in the effect of chloride concentration to K_d in the waters. For these rocks, the uncertainty is proposed to be covered by the same factors as for other nuclides: 20 for T-TGG and 50 for PGR.

The lower limit K_d values of chloride in the reference waters are calculated by dividing the best estimate K_d values by the uncertainty factor. The lower limit K_d values are presented in Tables I-7 to I-10.

Table I-6. *Factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	7
P-TGG	7
T-TGG	20
PGR	50

Table I-7. *The lower limit K_d (m^3/kg) values of iodine for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.6E-05**	**8.6E-05**	**2.9E-06**	**7.1E-07**	**5.7E-08**	**4.3E-06**	**4.3E-07**
10	8.6E-06	8.6E-06	6.0E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-8. *The lower limit K_d (m^3/kg) values of iodine for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.3E-05**	**4.3E-05**	**1.4E-06**	**3.6E-07**	**2.9E-08**	**2.1E-06**	**2.1E-07**
10	1.5E-07	1.5E-07	1.5E-07	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-9. *The lower limit K_d (m^3/kg) values of iodine for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E-05**	**1.0E-05**	**2.5E-07**	**5.0E-08**	**3.0E-09**	**4.5E-07**	**7.5E-09**
10	5.0E-08	5.0E-08	5.0E-08	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-10. *The lower limit K_d (m^3/kg) values of iodine for pegmatic granite PGR at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.0E-07**	**8.0E-07**	**2.0E-08**	**6.0E-09**	**4.0E-10**	**4.0E-08**	**4.0E-09**
10	5.4E-09	5.4E-09	5.4E-09	0.0E+00	0.0E+00	0.0E+00	0.0E+00

6.3 Sorption on clays

6.3.1 Source data

Kaolinite

Sorption of iodide on kaolinite was determined by Weerasooriya at al. (1998, 1999) as part of the work to model fluoride and anion adsorption on Rattola kaolinite. The R_d values were derived from values for fractional adsorption of iodide in $NaNO_3$ solutions (Figure 3 in Weerasooriya (1999)). The derived R_d values are given in Table I-11 and show a decrease of R_d with an increase of pH of the solution, in accordance with the change of positive surface charge of kaolinite (Bolland 1976). In $NaNO_3$ solutions, the R_d values decrease by a little less than a factor of two between pH 6 and pH 8. This decrease is much less than that in sorption of iodine on Olkiluoto mica gneiss in ALLMR water (Kulmala et al. 1998).

As in the case of chloride, the K_d values of iodide for kaolinite in the groundwaters are expected to have the same dependency of solution composition as sorption on mica gneiss. To take into account the higher BET surface area of the Rattola kaolinite than

that of the well-crystallised KGa-1b kaolinite, the R_d values are divided by two. The R_d at pH 8 in 0.01 M $NaNO_3$ is selected as the source data value, and it most probably does not overestimate sorption in ALLMR water.

Table I-11. *Sorption of iodide (1.1E-4 M) on Rattola (Sri Lanka) kaolinite.*

Kaolinite	BETN2 m^2/g	pH	solution M	R_d m^3/kg	R_d average
Rattola	24	6	$NaNO_3$ 1E-1	6.40E-03	5.17E-03
		7	$NaNO_3$ 1E-1	5.30E-03	
		8	$NaNO_3$ 1E-1	3.80E-03	
Rattola	24	6	$NaNO_3$ 1E-2	1.00E-02	8.57E-03
		7	$NaNO_3$ 1E-2	9.00E-03	
		8	$NaNO_3$ 1E-2	6.70E-03	
Rattola	24	6	$NaNO_3$ 4E-3	1.70E-02	1.33E-02
		7	$NaNO_3$ 4E-3	1.30E-02	
		8	$NaNO_3$ 4E-3	1.00E-02	

Illite

The R_d values of iodine on illite-rich OPA clay rock from Mont Terri and montmorillonite in Opalinus Clay porewater (ionic strength 0.34 M) at pH 7.5 in the in-house sorption measurements by Bradbury & Baeyens (2008a, 2008b) were about the same for these solids: $(3–4) \cdot 10^{-5}$ and $5 \cdot 10^{-4}$ m^3/ kg, respectively. The difference in K_d values is smaller than the difference in CEC values used for these solids.

Kaplan et al. (2000) give sorption distribution ratios for many minerals present in subsurface sediments and for illitic minerals. Sorption in 0.01 M $CaCl_2$ solution to layer silicates montmorillonite, chlorite, and vermiculite was much lower than to Morris illite. For this illite, the distribution value was 0.044 m^3/kg at pH 3.6 and 0.022 m^3/kg at pH 9.4.

The value measured in OPA groundwater simulant for the illite is used as the source data for estimation of the sorption of iodine on the Olkiluoto illite. Sorption of iodine on the rocks decreases with increase of pH and increase of ionic strength, as shown in Kulmala et al. (1998a). The pH of the brackish reference water OLBA and pH of the groundwater KR6_135_8 is 7.6, about the same as in OPA water, and the ionic strength of OLBA is 0.14 M, about half of that in the Opalinus water. By using the R_d values for OPA clay of Bradbury & Baeyens (2003a, 2003b) to Olkiluoto illite in OLBA we do not overestimate sorption of iodide. R_d values in the reference waters are taken to have the same ratios as those for the mica gneiss in the reference waters.

pH 10

As for the rocks at pH 10 the K_d value of 0 m^3/kg for I^- on illite in brackish and saline waters is suggested. For I^- in fresh ALLMR water, the K_d values for rocks at pH 8.8 and pH 10 have a ratio of 3. The same ratio is suggested for K_d values for illite at pH 8.8 and pH 10 respectively. For the glacial melting water OLGA, the same value as in ALLMR water is suggested.

6.3.2 Best estimate K_d values

The best estimate K_d values (m^3/kg) of iodine for kaolinite and illite are given in Tables I-12 and I-13.

Table I-12. *The best estimate K_d (m^3/kg) values of iodine for kaolinite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E-01**	**1.0E-01**	**3.4E-03**	**8.4E-04**	**6.7E-05**	**5.0E-03**	**5.0E-04**
10	1.1E-03	1.1E-03	1.1E-03	0.0E+00	0.0E+00	0.0E+00	0.0E+00

Table I-13. *The best estimate K_d (m^3/kg) values of iodine for illite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.6E-03**	**3.6E-03**	**1.2E-04**	**3.5E-05**	**2.4E-06**	**1.8E-04**	**1.8E-05**
10	4.0E-05	4.0E-05	4.0E-05	0.0E+00	0.0E+00	0.0E+00	0.0E+00

6.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{extrapol} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(I-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(I-2)}$$

Kaolinite

UF_{tot} = 15 (1.5 * 5 * 1 * 1 * 1 * 2) the total uncertainty factor.

UF_{source} = 1.5. The uncertainty factor of source data describes the uncertainty of the R_d values of the literature, from which the best estimate K_d values for illite were derived. The value of 1.5 covers the uncertainty in reading the graphs.

$UF_{extrapol}$ = 5. Extrapolation is made over large ionic strength and pH range. Between pH 6 and pH 8, the source data suggests a smaller decrease with increase of pH than used in the extrapolation, suggesting that we do not overestimate sorption.

UF_{CEC} = 1. Cation exchange capacity was not relevant here.

UF_{spec} = 1. The uncertainty of speciation factor is 1, because only one solution species exists in the reference waters.

UF_{pH} = 1. No corrections of K_d values with pH were made.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

Table I-14. *The lower limit K_d (m^3/kg) values of iodine for kaolinite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.7E-03**	**6.7E-03**	**2.3E-04**	**5.6E-05**	**4.5E-06**	**3.3E-04**	**3.3E-05**
10	7.3E-5	7.3E-5	7.3E-5	0.0E+00	0.0E+00	0.0E+00	0.0E+00

The lower limit K_d (m^3/kg) values of iodine for kaolinite in Olkiluoto geosphere are presented in Table I-14.

Illite

UF_{tot} = 26 (5 * 2 * 1.3 * 1 * 1 * 2) the total uncertainty factor.

UF_{source} = 5. The uncertainty factor of source data describes the uncertainty of the R_d values (iodine), from which the best estimate K_d values were derived. The value of 5 covers the uncertainty as proposed in Bradbury & Baeyens (2003).

$UF_{extrapol}$ = 2. Extrapolation is made over large ionic strength and pH range.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity. The cation exchange capacity (CEC) for pure illites is generally higher than that for OPA clay rocks. No conversion

for differences of CEC values was made due to the fact that low CEC minerals may also have had impact on sorption of iodide on the Opanlinus clay. The uncertainty in the source material compared with Olkiluoto site illite is taken into account in the uncertainty factor UF_{CEC} which was taken as 1.3.

UF_{spec} = 1. The uncertainty of speciation factor is 1, because only one solution species exists in the reference waters.

UF_{pH} = 1. No corrections of K_d values with pH were made.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m3/kg) values of iodine for illite in Olkiluoto geosphere are presented in Table I-15.

Table I-15. *The lower limit K_d (m^3/kg) values of iodine for illite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.4E-04**	**1.4E-04**	**4.6E-06**	**1.4E-06**	**9.2E-08**	**6.9E-06**	**6.9E-07**
10	1.5E-06	1.5E-06	1.5E-06	0.0E+00	0.0E+00	0.0E+00	0.0E+00

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7 CESIUM

7.1 Speciation

Cesium is in the groundwaters as a weakly hydrated cation Cs^+. Its sorption mechanism is cation exchange. Solubility of Cs in the waters is high. Groundwater analysis during site investigations in Olkiluoto has indicated that in saline groundwaters the Cs-concentration was generally lower than $1 \cdot 10^{-7}$ mol/L. The highest value was $1.5 \cdot 10^{-6}$ M. In shallow groundwaters waters the concentration was lower than $1 \cdot 10^{-8}$ M. (Hellä et al. 2014)

7.2 Sorption on rocks

7.2.1 Source data

R_d value of cesium for Olkiluoto tonalite in low ionic strength YD1 water (Nikula & Pinnioja 1981) was 3.7 m^3/kg and for biotite in Allard water 7.3 – 12 m^3/kg (Lindberg et al. 1983).

Huitti et al. (1998) determined sorption of Cs on crushed Olkiluoto tonalite, mica gneiss and granite in fresh Allard water and saline OLSO water as a function of pH and Cs-concentration. The pH dependence on the sorption on the Olkiluoto rocks was low, and on micas it is expected generally to be low (Cornell 1993). For clays, the R_d values increased/decreased with pH by about 8 % per pH unit from the R_d value at pH 7–8 (Nikula 1982). For the glacial melting water OLGA (pH 5.8), the K_d value is decreased for pH by 15% and for waters at pH 10, the K_d values are 15% higher than the values at pH 7–8.

The sorption of cesium on unaltered rocks correlates directly with the biotite content of a rock (Pinnioja et al. 1986). Cesium is also sorbed on all other micaceous minerals and clays. Sorption on low-CEC minerals like feldspars and quartz is low. Similarities in hydration of the alkaline metals Cs and K is well shown and affinity of mica minerals to Cs^+ sorption is only a little larger than for K^+. In groundwater, the main cations determining the ionic strength are Na^+, Ca^{2+}, Mg^{2+} and K^+. Selectivity of Na^+ and Ca^{2+} in sorption is much less than that of Cs^+ but owing their higher concentration they compete in sorption with cesium.

A mechanistic cation exchange sorption model by Kyllönen at al. (2008) for sorption of Cs on biotite was able to reproduce the experimental results in Huitti et al. (1998) for sorption of Cs in OLSR water on Olkiluoto mica gneiss. In the present work, this model was further applied to simulate sorption on Olkiluoto tonalite and granite in saline OLSR and fresh ALLMR waters, and on mica gneiss in ALLMR. The calculated values were in good agreement with the experimental values for the biotite rich mica gneiss. Impact of sorption on other micas (muscovite and chlorite) is not included in the model. The calculated K_d values are lower than experimental R_d values for the tonalite in ALLMR water and for the granite in OLSR. In all cases, the calculated values were not larger than the experimental R_d values (Table 3-6, Huitti et al. 1998).

The sorption experiments in Huitti et al. (1998) were used as the test case for using only the proportion and CEC of biotite for estimating K_d of Cs for mica gneiss and granite in fresh (ALLMO) water and saline (OLSR) water. Sorption is calculated using the geochemical programme, PHREEQC.

The cation exchange selectivity coefficients in Kyllönen et al. (2008) were used. The proportions of the three sorption sites were 93 %, 5 % and 2 %.

The proportion of biotite was 32 % for the mica gneiss, 6.6 % for the tonalite and 0.2% for the granite. The initial solution concentration in the experiments selected for calculation in ALLMO water was $1.1 \cdot 10^{-5}$ M for the mica gneiss and tonalite and $1.1 \cdot 10^{-6}$ M for the granite. For OLSR water, the initial Cs concentration was $1.1 \cdot 10^{-6}$ M in all cases. In these experiments, the equilibrium Cs solution concentrations are in the range of Cs concentration in the Olkiluoto groundwaters (Hellä et al. 2014). The calculated R_{dCALC} values and the experimental R_{dEXP} values for the crushed rocks are given in Table 3-6.

The calculated R_{dCALC} values for mica gneiss are at the upper limit of experimental R_{dEXP} values both in ALL and OLSR water. For tonalite in ALL water, the R_{dEXP} values are about 1.5 to 2.4 times higher than the derived R_{dCALC} value, but in OLSR the R_{dEXP} and R_{dCALC} values are the same. For the granite, the R_{dEXP} value is about the same as the R_{dCALC} value. In OLSR, the derived R_{dCALC} value for granite is much lower than the R_{dEXP} value. This suggests that in the low biotite content granites the sorption on other minerals may be more important than sorption on biotite, as was also the case in the determination of sorption to PGR by electromigration.

Table Cs-1. *Calculated R_{dCALC} values of Cs for Olkiluoto mica gneiss and granite. Experimental R_{dEXP} values for crushed rock are from Huitti et al. (1998). CEC = calculated cation exchange capacity of the rock. MGN = mica gneiss, TON = tonalite (granodiorite), GR = granite.*

Water	Rock	Biotite (%)	CEC (μeq/g)	Cs initial (M)	Cs equil. (M)	$R_{d\,EXP}$ (m^3/kg)	R_{dCALC} (m^3/kg)
ALLMO	MGN	32	4.8	$1.1 \cdot 10^{-5}$	$1.65 \cdot 10^{-7}$	0.56- 0.72	0.77
ALLMO	TON	6.6	0.99	$1.1 \cdot 10^{-5}$	$4.4 \cdot 10^{-7}$	0.23 - 0.38	0.10
ALLMO	GR	0.2	0.03	$1.1 \cdot 10^{-6}$	$7.7 \cdot 10^{-8}$	0.14 - 0.15	0.12
OLSR	MGN	32	4.8	$1.1 \cdot 10^{-6}$	$5.0 \cdot 10^{-8}$	0.19 -0.26	0.26
OLSR	TON	6.6	0.99	$1.1 \cdot 10^{-6}$	$2.0 \cdot 10^{-7}$	0.042 - 0.051	0.049
OLSR	GR	0.2	0.03	$1.1 \cdot 10^{-6}$	$3.1 \cdot 10^{-7}$	0.015 - 0.016	0.002

Calculation of K_d values

The variables used in the model calculations were Cs-concentration in the waters and the biotite content of the rock types. The equilibrium Cs concentration used in the calculations was $1 \cdot 10^{-7}$ mol/L and $1 \cdot 10^{-6}$ mol/L to simulate the groundwaters. These values are at the high end of the Cs concentrations measured in the Olkiluoto groundwaters. The values used for biotite content were the mean and the mean minus

the standard deviation (= lower limit of biotite content). In PGR, the biotite concentration is low and its relative standard deviation is high. To have meaningful rock conditions for calculation, the lower value was taken to be 0.1 %. The accessibility of CEC in the P-TGG rock is also here assumed to be 7.5 μeq/g biotite (50 % of 15 μeq/g biotite).

7.2.2 Best estimate K_d values

The K_d values for the glacial melting water (OLGA/OLGO) and fresh groundwater ALLMR are selected based on Cs equilibrium concentration $1 \cdot 10^{-7}$ M. The values of ALLMO water are the same as the values of ALLMR water due to them having almost the same ionic composition. The K_d values for the brackish waters (OLBA, KR4_81_1) and saline waters (OLSR/OLSO, KR20_465_1) are selected based on Cs equilibrium concentration of $1 \cdot 10^{-6}$ M. The best estimate values are for mean biotite content of the rocks. The values are collected in Tables Cs-2 – Cs-5.

Table Cs-2. *Best estimate K_d values (m^3/kg) of Cs for mica gneiss T-MGN. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.3E+00**	**1.3E+00**	**8.4E-01**	**9.0E-02**	**8.0E-02**	**1.2E-01**	**9.5E-02**
10	1.7E+00	1.7E+00	9.7E-01	1.0E-01	9.0E-02	1.4E-01	1.1E-01

Table Cs-3. *Best estimate K_d values (m^3/kg) of Cs for P series granodiorite gneiss P-TGG. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-01**	**6.0E-01**	**4.2E-01**	**4.5E-02**	**4.0E-02**	**6.0E-02**	**4.7E-02**
10	8.0E-01	8.0E-01	4.8E-01	5.0E-02	4.5E-02	7.0E-02	5.5E-02

Table Cs-4. *Best estimate K_d values (m^3/kg) of Cs for T series granodiorite gneiss T-TGG. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.8E-01**	**4.8E-01**	**3.2E-01**	**3.5E-02**	**3.0E-02**	**4.6E-02**	**3.7E-02**
10	6.0E-01	6.0E-10	3.7E-01	4.0E-02	3.5E-02	5.0E-02	4.3E-02

Table Cs-5. *Best estimate K_d values (m^3/kg) of Cs for pegmatic granite PGR. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E-02**	**5.0E-02**	**3.5E-02**	**4.0E-03**	**3.0E-03**	**5.0E-03**	**4.0E-03**
10	6.2E-02	6.2E-02	4.0E-02	5.0E-03	3.0E-03	6.0E-03	5.0E-03

7.2.3 Lower limit K_d values

The lower limit values are for the lower limit biotite content of the rocks. The lower limit K_d values (m^3/kg) of Cs for the reference rocks are presented in Tables Cs-6 – Cs-9.

Table Cs-6. *The lower limit K_d values (m^3/kg) of Cs for mica gneiss T-MGN. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.1E-01**	**8.1E-01**	**5.5E-01**	**5.4E-02**	**4.8E-02**	**7.3E-02**	**5.7E-02**
10	1.4E+00	1.4E+00	6.3E-01	6.0E-02	6.0E-02	8.0E-02	7.0E-02

Table Cs-7. *The lower limit K_d values (m^3/kg) of Cs for P series granodiorite gneiss P-TGG. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.1E-01**	**4.1E-01**	**2.8E-01**	**2.7E-02**	**2.4E-02**	**3.7E-02**	**2.9E-02**
10	5.3E-01	5.3E-01	3.2E-01	3.0E-02	3.0E-02	4.0E-02	3.5E-02

Table Cs-8. *The lower limit K_d values (m^3/kg) of Cs for T series granodiorite gneiss T-TGG. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.0E-02**	**4.0E-02**	**3.0E-02**	**3.0E-03**	**2.6E-03**	**4.0E-03**	**3.0E-03**
10	5.2E-02	5.2E-02	3.0E-02	3.0E-03	3.0E-03	4.0E-03	3.0E-03

Table Cs-9. *The lower limit K_d values (m^3/kg) of Cs for pegmatic granite PGR. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**6.0E-03**	**4.0E-03**	**4.0E-04**	**3.0E-04**	**6.0E-04**	**4.0E-04**
10	7.8E-03	7.8E-03	5.0E-03	5.0E-04	4.0E-04	5.0E-04	4.0E-04

7.3 Sorption on clays

7.3.1 Source data

Kaolinite

The best estimate K_d values for kaolinite were derived from sorption isotherm of Cs on kaolinite KGa-1b in 1 mM $NaNO_3$ solution (Puukko & Hakanen 1999). No cation selectivity coefficients for exchange Cs and the main groundwater cations to kaolinite were found in the literature.

Jeong (2001) determined sorption of Cs on Georgia kaolinite in $1 \cdot 10^{-5}$ M to 0.1 M solutions of NaCl, KCl, $CaCl_2$ and $MgCl_2$. The solid to solution ratio was 0.33 g/10 mL. In equimolar NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions, the sorption of Cs on kaolinite followed the order Na>Ca=Mg>K. At higher ionic concentrations, sorption of Cs in NaCl solution was about two times higher than in $CaCl_2$ and $MgCl_2$ solutions of the same molarity as the NaCl solutions. This suggests that the selectivity of Cs for kaolinite is the same for Na^+ and the divalent earth alkaline cations of the same normality. A robust estimation is made that the effect of Na and earth alkaline cations on sorption of Cs is the same per charge equivalent concentration, and that there is no selectivity between Cs, Na and earth alkalines in sorption to kaolinite. In the brackish and saline Olkiluoto groundwaters and groundwater simulants, the Na concentration is about two times higher than the total earth alkaline molar concentration. The conversion factor to derive the R_d values in the groundwater simulants and groundwaters is the ratio of in Na-concentration in experiment of Puukko & Hakanen (1999) (1mM) divided by the cationic charge concentration (CAT) in a groundwater. Table Cs-10 gives R_d values derived to Ca+Mg+Na-charge concentration in the reference groundwaters and groundwater simulants. Accuracy of deriving these R_d values is low, especially for the saline waters, due to their higher ionic strength than that used in Jeong (2001) and to which sorption was extrapolated. The results suggest that in saline waters the competition in sorption with Cs is by the earth alkaline ions, and that also the competition per unit charge is probably higher than by Na. At pH 3 in 1mM $NaNO_3$, the R_d value was $8.5 \cdot 10^{-2}$ m^3/kg for Cs equilibrium concentration $3.7 \cdot 10^{-6}$ M. Compared with R_d value $1 \cdot 10^{-1}$ m^3/kg at pH 8, the authors conclude that the pH dependence of sorption of Cs to kaolinite is small.

Groundwater conditions in the literature studies of sorption of Cs on kaolinite are ill-defined. The K_d values of Cs for kaolinite derived using the ratio of total cationic charge

for correcting the data in Puukko & Hakanen (1999) are low compared to the values in Torstenfelt et al. (1982), Tamura (1972) and Ticknor et al. (1991).

Illite

Sorption of Cs on IMt-1 illite was calculated using the cation exchange selectivity coefficients for Na/K, Na/Cs and Na/Ca exchange for illite in Poinssot et al. (1999). The sorption of Cs at $1 \cdot 10^{-6}$ M equilibrium concentration of the waters on the illite was calculated.

Table Cs-10. *The cesium equilibrium concentration (Cs M) and R_d values of Cs for kaolinite in the source data of Puukko and Hakanen (1999) and R_d (m^3/kg) values of Cs derived to the groundwaters at pH 8-10.*

	1mM $NaNO_3$	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
CAT	1.0	0.085	3.1	410	110	24	191
Cs M							
3.33E-05	1.00E-01	1.2E+00	3.3E-02	2.4E-04	9.1E-04	4.2E-03	5.2E-04
2.22E-06	1.75E-01	2.1E+00	5.6E-02	4.3E-04	1.6E-03	7.3E-03	9.2E-04
1.59E-07	2.65E-01	3.1E+00	8.6E-02	6.5E-04	2.4E-03	1.1E-02	1.4E-03
1.33E-08	3.25E-01	3.8E+00	1.1E-01	7.9E-04	2.9E.03	1.4E-02	1.7E-03
1.25E-12	3.50E-01	4.1E+00	1.1E-01	8.5E-04	3.2E-03	1.5E-02	1.8E-03
CAT = cationic charge concentration (cmmol/L)							

The cation exchange capacity of the IMt-1 illite is reported to be 170 meq/kg (Missana et al. 2008) and 250 meq/kg (Polusebova & Nir 1999). Ames et al. (1983b) give a CEC of 250 meq/kg for Cs in Fithian Illinois illite. The CEC used in the calculations was 225 meq/kg as determined for Cs in du Puy illite by Baeyens & Bradbury (2004). The proportions of site capacities in Bradbury & Baeyens (2003) were used. Sorption is the same at pH 6-10. In 0.1 M $NaClO_4$ the K_d of Cs for the Na-illite was about 30 m^3/kg and 0.3 m^3/kg in $1.6 \cdot 10^{-8}$ M and $7.4 \cdot 10^{-4}$ M Cs concentration, respectively (Poinssot et al. 1999). The K_d values of Cs for the illite in the groundwater in $1 \cdot 10^{-6}$ M Cs concentration are given in Table Cs-12. The same values are proposed for the waters at pH 10.

7.3.2 Best estimate K_d values

The best estimate K_d values of cesium for kaolinite and illite in the Olkiluoto geosphere are presented in Tables Cs-11 and Cs-12. For kaolinite the K_d values are for Cs concentration $2 \cdot 10^{-6}$ M. Because of high uncertainty in the way the R_d values were derived, the best estimate K_d value in the glacial melting waters (OLGA and OLGO) is proposed to be one tenth of the calculated R_d value.

Table Cs-11. *Best estimate K_d values (m^3/kg) of cesium for kaolinite in Olkiluoto geosphere. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.1E-01**	**2.1E-01**	**6.0E-02**	**2.0E-03**	**4.0E-04**	**1.0E-02**	**1.0E-03**
10	2.1E-01	2.1E-01	6.0E-02	2.0E-03	4.0E-04	1.0E-02	1.0E-03

Table Cs-12. *Best estimate K_d values (m^3/kg) of cesium for illite in Olkiluoto geosphere. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.3E+01**	**1.3E+01**	**7.8E+00**	**7.5E+00**	**7.5E+00**	**7.5E+00**	**7.3E+00**
10	1.3E+01	1.3E+01	7.8E+00	7.5E+00	7.5E+00	7.5E+00	7.3E+00

7.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source}*UF_{model}*UF_{CEC}*UF_{spec}*UF_{pH}*UF_{lab/field} \quad \text{(Cs-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Cs-2)}$$

Kaolinite

The total uncertainty factor UF_{tot} of cesium for kaolinite in Olkiluoto geosphere is 1.40*2.00*2.00= 5.60 . Lower limit Kd values are shown in Table Cs-13.

The uncertainty factor of source data (UF_{source}) describes the uncertainty of the R_d values, from which the best estimate K_d values for kaolinite were derived. The R_d values were from Puukko & Hakanen (1999). The R_d value at Cs concentration $2 \cdot 10^{-6}$ M is 0.175 ± 0.05 m^3/kg and the UF_{source} is thus 1.4.

In saline waters, the Na concentration is roughly two times higher than Ca^{2+} / Mg^{2+} concentration. The R_d values corresponding to only Ca^{2+} / Mg^{2+} concentration are lower than those for Na-concentration by a factor of about two. This suggests that the earth alkaline concentration affects the R_d values about four times more (two times charge equivalents) than Na. In the calculation of K_d values, the ratio of total cationic charge of

waters was used. A factor of two is suggested to cover the uncertainty in this approach and so the UF_{model} is 2.

No cation exchange capacity corrections were used and so the UF_{CEC} is 1.

The sorbing species of cesium is Cs^+ and so the UF_{spec} is 1.

Sorption of Cs at pH 8-10 in $1 \cdot 10^{-3}$ M $NaNO_3$ was about two times higher than at pH 3. The nominal pH values of the waters are near the pH of source data (pH 8-10) and no correction is made for pH. The UF_{pH} is 1.

The scaling up from laboratory data to whole clay matrix ($UF_{lab/field}$) is covered by the factor 2.

Illite

The total uncertainty factor UF_{tot} of cesium for illite in the Olkiluoto geosphere is 1.40*2.00*1.3.*2.00= 7.3. Lower limit Kd values are shown in Table Cs-14.

The uncertainty factor of the source data (UF_{source}) describes the uncertainty of the R_d values, from which the best estimate K_d values for kaolinite were derived. The R_d values were from the literature (Poinssot et al. 1999). The UF_{source} is 1.4.

In saline waters, the Na concentration is roughly two times higher than Ca^{2+} / Mg^{2+} concentration. The R_d values corresponding to only Ca^{2+} / Mg^{2+} -concentration are lower than those for Na-concentration by a factor of about two. This suggests that the earth alkaline concentration affects the R_d values about four times more (two times charge equivalents) than Na. In the calculation of K_d values, the ratio of total cationic charge of waters was used. A factor of two is suggested to cover the uncertainty in this approach and so the UF_{model} is 2.

The cation exchange capacity (CEC) for illite is generally higher than for kaolinite. The uncertainty in the source material compared with the Olkiluoto site illite is taken into account in the uncertainty factor UF_{CEC} which was taken as 1.3, since the CEC of source data illite and Olkiluoto illite may be significantly different (Bradbury & Baeyens 2003c, Missana et al. 2008).

The sorbing species of cesium is Cs^+ and so the UF_{spec} is 1. This is omitted from Table Cs-15.

No corrections of pH for K_d values were made and so the UF_{pH} is 1.

The scaling up from laboratory data to whole clay matrix ($UF_{lab/field}$) is covered by the factor 2.

Table Cs-13. *The lower limit K_d values (m^3/kg) of cesium for kaolinite in Olkiluoto geosphere. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.0E-02**	**4.0E-02**	**1.1E-02**	**3.6E-04**	**7.1E-05**	**1.8E-03**	**1.8E-04**
10	4.0E-02	4.0E-02	1.1E-02	3.6E-04	7.1E-05	1.8E-03	1.8E-04

Table Cs-14. *The lower limit K_d values (m^3/kg) of Cs for illite in Olkiluoto geosphere. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.8E+00**	**1.8E+00**	**1.1E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**
10	1.8E+00	1.8E+00	1.1E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00

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8 SILVER

The natural Ag groundwater concentrations are of the order of $1 \cdot 10^{-9}$ M to $1 \cdot 10^{-8}$ M (Bruno et al. 1997, Newcomb & Rimstidt 2002). The Ag concentration in Finnish drilled well waters is lower than $1 \cdot 10^{-8}$ M (Gustavsson et al. 2001).

8.1 Speciation

Speciation of silver is not pH dependent in the reference waters owing to the weak hydrolysis of the Ag^+ ion. The important species are the Ag^+ cation and the chloride complexes. Only in the brackish groundwater KR4_81_1 is there an impact of carbonato complexation at high pH. The fraction of Ag^+ decreases from 95.5 % in glacial meltwater OLGA to 30 % in fresh reference water ALLMR, 3.4 % in KR4_81_1, 0.34 % in brackish reference water OLBA, $2 \cdot 10^{-2}$ % in saline groundwater KR20_465_1 and $3 \cdot 10^{-3}$ % in saline reference water OLSR. The chloride complexes are the uncharged AgCl and the anionic $AgCl_2^-$, $AgCl_3^{2-}$ and $AgCl_4^{3-}$ (Figures Ag-1 – Ag-3).

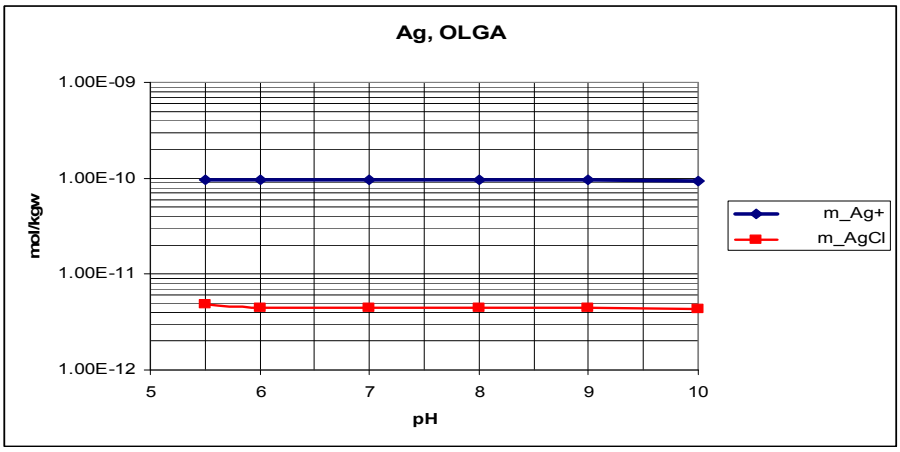

Figure Ag-1. *Ag species in glacial meltwater OLGA.*

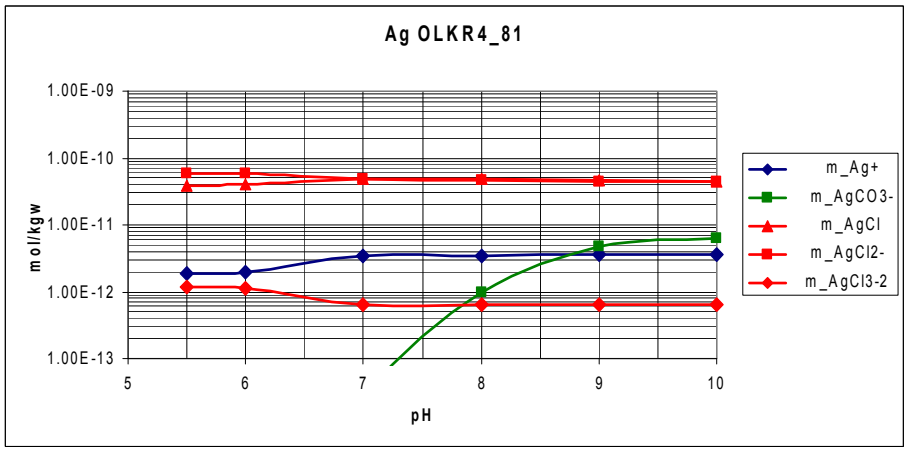

Figure Ag-2. *Ag species in brackish groundwater KR4_81_1.*

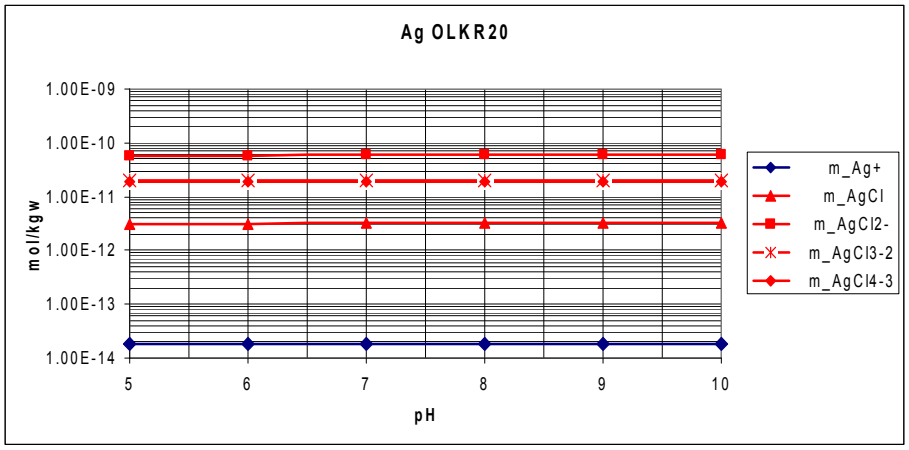

Figure Ag-3. *Ag species in saline groundwater KR20_465_1.*

8.2 Sorption on rocks

8.2.1 Source data

No relevant data for sorption of Ag on crystalline rocks is available in the open literature. Khan et al. (1995) studied the sorption of silver in $NaNO_3$ solution for bentonite and found no pH dependence on sorption at pH 4 to pH 7. In 0.1 M $NaNO_3$ solution, the main Ag species (97 %) is Ag^+ in $NaNO_3$ solution. The sorption edge in these non-complexing conditions for Ag^+ was at pH 7.5 - pH 9. For Ag concentration of $1 \cdot 10^{-9}$ M, the R_d value was $32 \cdot 10^{-3}$ m^3/kg for bentonite (CEC 77 meq/100g, BET/N_2 surface area 34 m^2/g) at pH 6.5.

According to Hernandez et al. (2003), the ionic strength in $NaNO_3$ solution does not affect either sorption kinetics or sorption thermodynamics on quartz. The R_d value for Ag for the silty soil (CEC 55 meq/100g) at pH 7.47 in $NaNO_3$ solution was $36 \cdot 10^{-3}$ m^3/kg. This is in fair agreement with the R_d value of Khan et al. (1995) for the bentonite, and suggests that CEC can be used for the conversion of R_d values for bentonite to R_d for biotite.

8.2.2 Best estimate K_d values

For the calculation of K_d values for the rocks, the R_d value for bentonite at pH 6.5 in Khan et al. (1995) is applied. The ratios of the CEC value and BET/N_2 surface area for the bentonite in Khan et al. (1995) to the CEC value used here for Olkiluoto biotite (1.5 meq/100g, Kyllönen et al. (2008)) and the BET/N_2 surface area (0.8 m^2/g) are about 50 and 43, respectively. The R_d value of Ag to biotite in non-complexing solution is calculated by using the CEC ratio of biotite to bentonite R_d value and is $0.64 \cdot 10^{-3}$ m^3/kg (=R_d/SA=1/50*$32 \cdot 10^{-3}$ m^3/kg).

It is assumed here that the only sorbing species is the Ag^+ cation. The sorption mechanism is assumed to be cation exchange. The K_d values for the reference rocks in the reference waters are derived by using the above calculated R_d for biotite ($0.64 \cdot 10^{-3}$

m^3/kg), the proportion of biotite in the rock and the fraction of Ag^+ of the total Ag in the water. No other correction for water compositions is made. For waters at pH higher than 7.5, the calculated values are most probably conservative, because the impact of possible surface complexation could not be taken into account owing to the fact that R_d values for trace concentrations of Ag at pH higher than 6.5 were not available. For Olkiluoto P-series tonalite granodiorite granite gneiss P-TGG it is assumed that the accessible CEC of biotite is 0.75 meq/100 g, half of that in the other rocks. The best estimate K_d values are given in Tables Ag-1 – Ag-4.

Table Ag-1. *Best estimate K_d values (m^3/kg) of silver for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.4E-04**	**1.4E-04**	**5.0E-05**	**5.0E-07**	**4.0E-09**	**5.0E-06**	**3.8E-08**
10	1.4E-04	1.4E-04	5.0E-05	5.0E-07	4.0E-09	5.0E-06	3.8E-08

Table Ag-2. *Best estimate K_d values (m^3/kg) of silver for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E-05**	**7.0E-05**	**2.5E-05**	**2.5E-07**	**2.0E-09**	**2.5E-06**	**1.4E-08**
10	7.0E-05	7.0E-05	2.5E-05	2.5E-07	2.0E-09	2.5E-06	1.4E-08

Table Ag-3. *Best estimate K_d values (m^3/kg) of silver for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-05**	**6.0E-05**	**2.0E-05**	**2.0E-07**	**2.0E-09**	**2.0E-06**	**2.0E-08**
10	6.0E-05	6.0E-05	2.0E-05	2.0E-07	2.0E-09	2.0E-06	2.0E-08

Table Ag-4. *Best estimate K_d values (m^3/kg) of silver for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-06**	**6.0E-06**	**2.0E-06**	**2.0E-08**	**2.0E-10**	**2.0E-07**	**2.0E-09**
10	6.0E-06	6.0E-06	2.0E-06	2.0E-08	2.0E-10	2.0E-07	2.0E-09

8.2.3 Lower limit K_d values

The source R_d data (Khan et al. 1995) was determined at pH 6.5. For glacial meltwater OLGA (pH 6), no correction for pH is needed, as shown by data in Khan et al. (1995). In the calculation of the best estimate values in Table Ag-1, no uncertainty in the conversion of R_d values from bentonite to biotite was taken into account. The properties of the bentonite are well described and the ratio of CEC values and surface areas between the bentonite and biotite is about the same. The uncertainty in the K_d values is due to uncertainties in the conversion of R_d for bentonite to R_d for biotite and to R_d to K_d for the rock. The total error is difficult to quantitate. It is regarded as reasonable that the lower limit values are calculated for the rocks by dividing the best estimate values by uncertainty factors calculated for each rock type (Table Ag-5). The lower limit K_d values are shown in Tables Ag-6 – Ag-9.

Table Ag-5. *The uncertainty factors of silver for rocks. T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

Reference rock	Factor for random error calculation
T-MGN. P-TGG	20
T-TGG	20*
PGR	50*
*error propagation using the errors in the mica contents and BET/N_2 (surface area) of micas and crushed rock yield unrealistically low correction factor for T-MGN and PGR. Omitting the error in BET/N_2 of crushed rock, the factor for T-TGG is 7 and for PGR 43.	

Table Ag-6. *Lower limit K_d values (m^3/kg) of silver for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E-06**	**7.0E-06**	**2.0E-06**	**2.0E-08**	**2.0E-10**	**2.0E-07**	**2.0E-09**
10	7.0E-06	7.0E-06	2.0E-06	2.0E-08	2.0E-10	2.0E-07	2.0E-09

Table Ag-7. *Lower limit K_d values (m^3/kg) of silver for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.5E-06**	**3.5E-06**	**1.0E-06**	**1.0E-08**	**1.0E-10**	**1.0E-07**	**1.0E-09**
10	3.5E-06	3.5E-06	1.0E-06	1.0E-08	1.0E-10	1.0E-07	1.0E-09

Table Ag-8. *Lower limit K_d values (m^3/kg) of silver for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E-06**	**2.0E-06**	**1.0E-06**	**1.0E-08**	**1.0E-10**	**1.0E-07**	**1.0E-09**
10	2.0E-06	2.0E-06	1.0E-06	1.0E-08	1.0E-10	1.0E-07	1.0E-09

Table Ag-9. *Lower limit K_d values (m^3/kg) of silver for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E-07**	**1.0E-07**	**4.0E-08**	**4.0E-10**	**4.0E-12**	**4.0E-09**	**4.0E-11**
10	1.0E-07	1.0E-07	4.0E-08	4.0E-10	4.0E-12	4.0E-09	4.0E-11

8.3 Sorption on clays

8.3.1 Source data

No in-house data or data in the open literature for sorption of Ag on clays in groundwaters is available. Silver sorption on kaolinite in a $5 \cdot 10^{-3}$ – $1 \cdot 10^{-1}$ M $AgNO_3$ solution (0.4g/25mL) was reported by Daniels & Rao (1983). They assumed a kaolinite CEC of 5-9 meq/100g and a BET/N_2 value of 13.52 m^2/g (Fripat 1964 in Daniels & Rao 1983). The calculated R_d in a $5 \cdot 10^{-3}$ M $AgNO_3$ solution was $4.24 \cdot 10^{-3}$ m^3/kg. This is in accordance with the results for bentonite by Khan et al. (1995), where the R_d value was $3.2 \cdot 10^{-2}$ m^3/kg in a $1 \cdot 10^{-9}$ M silver concentration at pH 6.5 (CEC 77 meq/100g, BET/N_2 34 m^2/g).

8.3.2 Best estimate K_d values

It is assumed here that the only sorbing species is the Ag^+ cation. The sorption mechanism is assumed to be cation exchange.

The K_d values for the kaolinite in the reference waters are calculated by using the R_d of source data (Daniels & Rao 1983). The speciation was taken into account by multiplying by the fraction of Ag^+ of the total Ag in the water. The CEC for kaolinite KGa-1b is 2-4 meq/100g, about half of the lower limit reported by Daniels & Rao (1983). For the sake of conservatism, the R_d values are divided by two. No correction for water compositions is made. For waters at pH higher than 7.5, the calculated values are most probably conservative because the impact of possible surface complexation could not be taken into account owing to the fact that there were no available R_d values for the trace concentrations of Ag at pH higher than 6.5. The best estimate K_d values are given in Table Ag-10. For other waters, the K_d value is proportional to its chloride concentration.

K_d values for the illite were converted from R_d values on bentonite in 0.1 M $AgNO_3$ solution at pH 4-7 (Khan et al. 1995) using the ratio of CEC values for the bentonite (770 meq/kg) and IMt-1 illite (170 meq/kg). These values were further converted to K_d values in the groundwaters, assuming that Ag^+ is the only sorbing species. The K_d values are given in Table Ag-11.

Table Ag-10. *Best estimate K_d values (m^3/kg) of silver for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.0E-03**	**2.0E-03**	**6.0E-04**	**6.0E-04**	**7.2E-06**	**6.4E-08**	**6.4E-08**	**7.2E-05**	**4.2E-07**
10	2.0E-03	2.0E-03	6.0E-04	6.0E-04	7.2E-06	6.4E-08	6.4E-08	7.2E-05	4.2E-07

Table Ag-11. *Best estimate K_d values (m^3/kg) of silver for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**6.7E-03**	**6.7E-03**	**2.1E-03**	**2.1E-03**	**2.4E-05**	**2.1E-07**	**2.1E-07**	**2.4E-04**	**1.4E-06**
10	6.7E-03	6.7E-03	2.1E-03	2.1E-03	2.4E-05	2.1E-07	2.1E-07	2.4E-04	1.4E-06

8.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays at Olkiluoto is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab\_field} \quad \text{(Ag-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) value by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Ag-2)}$$

Kaolinite

UF_{source} = 1.6 (as in Bradbury & Baeyens 2003). The source data for K_d values is solely from the literature. This includes also the uncertainty that the source data were from $AgNO_3$ solution (Daniels & Rao 1983) and derived for reference waters.

UF_{model} = 1. No model was used.

UF_{CEC} = 1. Since the source data were downscaled to well-crystallised kaolinite KGa-1b, there is no need for an uncertainty factor concerning differences between source data and reference conditions.

UF_{spec} = 1.4 It is assumed here that the chloride complexes of Ag are non-sorbing and the only sorbing species is the Ag^+ cation. The speciation was taken into account by multiplying K_d values by the fraction of Ag^+ of the total Ag in the reference water.

UF_{pH} = 1. There is no pH dependency in the best estimate K_d values because the possible impact of surface complexation was omitted.

UF_{lab_field} = 2. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} = 4.5 (1.6*1*1*1.4*1*2).

The lower limit K_d values for kaolinite at Olkiluoto are presented in Table Ag-12.

Table Ag-12. *Lower limit K_d values (m^3/kg) of silver for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.5E-04**	**4.5E-04**	**1.4E-04**	**1.4E-04**	**1.6E-06**	**1.4E-08**	**1.4E-08**	**1.6E-05**	**9.4E-08**
10	4.5E-04	4.5E-04	1.4E-04	1.4E-04	1.6E-06	1.4E-08	1.4E-08	1.6E-05	9.4E-08

Illite

Most of the uncertainty factors for illite are the same as for kaolinite.

UF_{CEC} = 1.3. There is an uncertainty in the CEC values of the bentonite source material and the IMt-1 illite compared with Olkiluoto site illite (see Chapter 3).

UF_{tot} = 5.8 (1.6*1*1.3*1.4*1*2).

The lower limit K_d values for illite at Olkiluoto are presented in Table Ag-13.

Table Ag-13. *Lower limit K_d values (m^3/kg) of silver for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.2E-03**	**1.2E-03**	**3.6E-04**	**3.6E-04**	**4.1E-06**	**3.6E-08**	**3.6E-08**	**4.1E-05**	**2.4E-07**
10	1.2E-03	1.2E-03	3.6E-04	3.6E-04	4.1E-06	3.6E-08	3.6E-08	4.1E-05	2.4E-07

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9 BERYLLIUM

Beryllium is the lightest alkaline earth element. Its mean abundance in the Earth's crust is 2.6 mg/kg. The concentration of stable beryllium (Be-9) in sea water has been reported to vary from $1 \cdot 10^{-11}$ M at greater depth (Kusakabe et al. 1987) to $5 \cdot 10^{-8}$ M in inland seas (Ishibashi et al. 1956). No Be concentration has been determined in the Olkiluoto groundwaters. The median Be concentration measured in Finnish drilled wells (drinking water) was lower than $1 \cdot 10^{-8}$ M and was rarely more than $1 \cdot 10^{-7}$ M (Lahermo et al. 2002). Concentrations were commonly higher in waters with high fluoride concentrations in wells in regions of granitic bedrock.

9.1 Speciation

The oxidation state of Be is +2 as for the other alkaline earths, Mg, Ca, Sr, Ba and Ra in environment. The chemical nature of Be is more covalent than ionic, unlike the other alkaline earths that are ionic.

The Thermo_Chimie 7b TDB does not include Be (ANDRA 2009). The solubility and speciation of Be was calculated with the PHREEQC programme using the MINTEQ v.4 thermodynamic database (2005) for soluble species. The solubility limiting phase was assumed to be crystalline $Be(OH)_2(\alpha)$. The values for the solubility product of $Be(OH)_2(\alpha)$ were adopted from Gilbert & Garret (1956), also adopted in Baes & Mesmer (1986). The solubility and the accompanied Be species in saline reference water OLSR, brackish groundwater KR4_81_1 and glacial OLGA meltwater are presented in Figures Be-1 – Be-3. In the saline and brackish waters, Be-fluorido and Be-chlorido complexation increased the calculated solubility at low pH. The lowest solubility is in all waters at pH 8–9 and is about $2 \cdot 10^{-7}$ M. Using $Be(OH)_2(am)$ as the solubility controlling phase raises the lowest Be concentration by a factor of two to $6 \cdot 10^{-7}$ M at pH 8–9.

The speciation of Be in the waters is given in Figures Be-4 – Be-7. The calculations indicate that the main species at pH 6–10 are hydroxo complexes. At lower pH in the saline and brackish waters, Be-fluorido complexes are abundant.

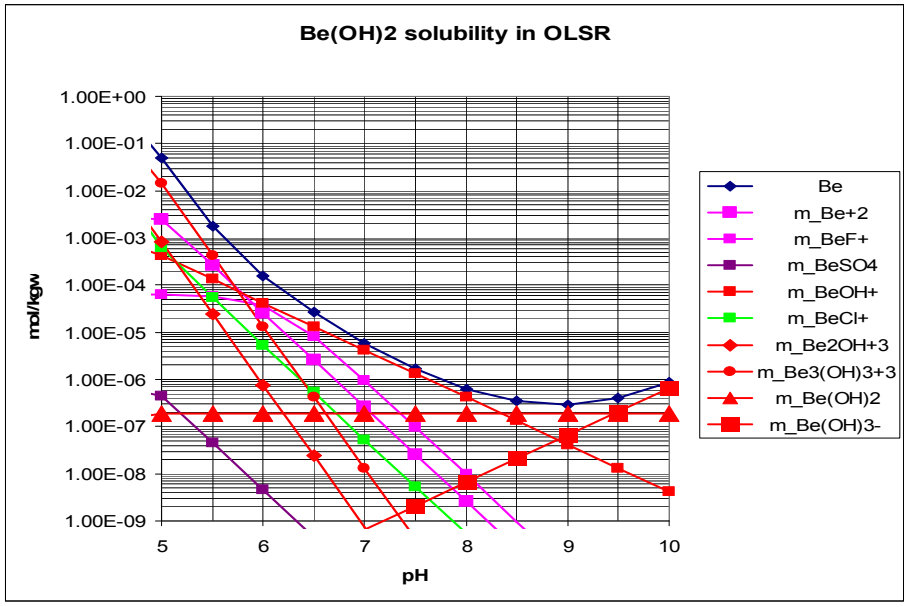

Figure Be-1. *Solubility of $Be(OH)_2(\alpha)$ in saline OLSR reference water.*

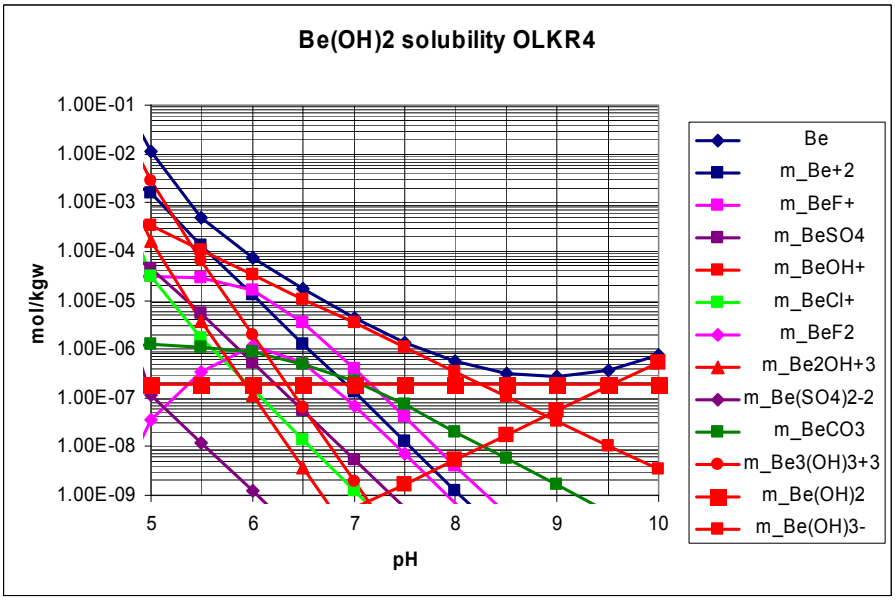

Figure Be-2. *Solubility of $Be(OH)_2(\alpha)$ in brackish KR4_81_1 groundwater.*

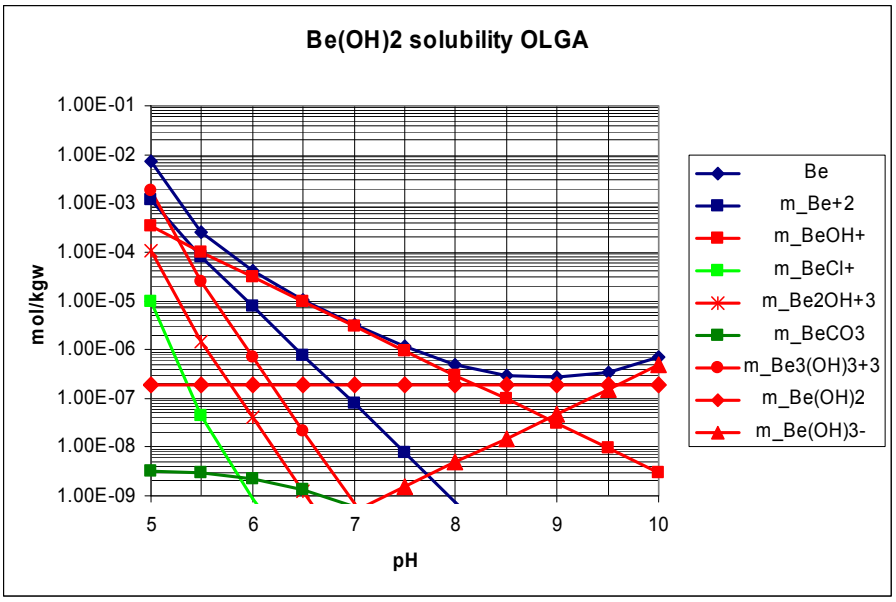

Figure Be-3. *Solubility of $Be(OH)_2(\alpha)$ in glacial OLGA meltwater.*

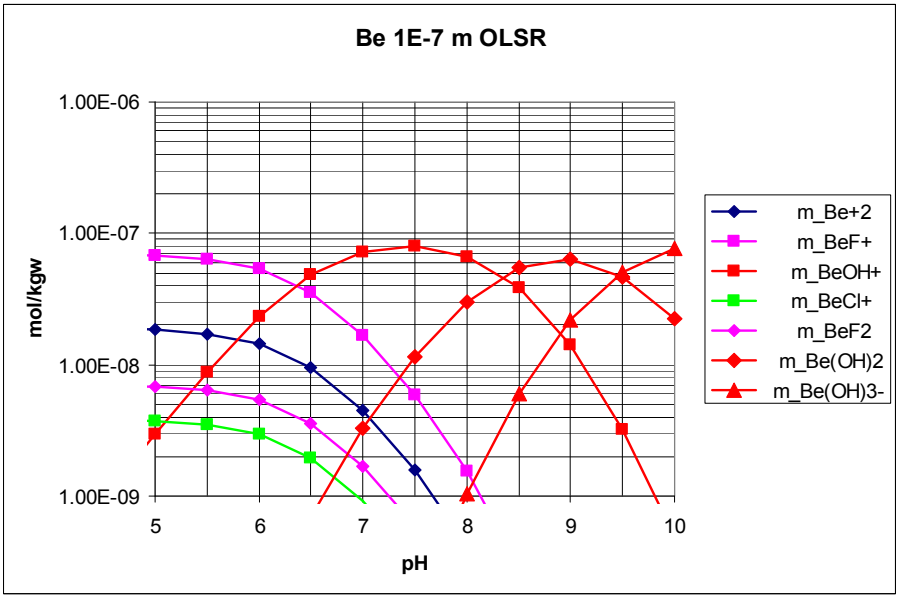

Figure Be-4*. Speciation of Be in saline OLSR reference water.*

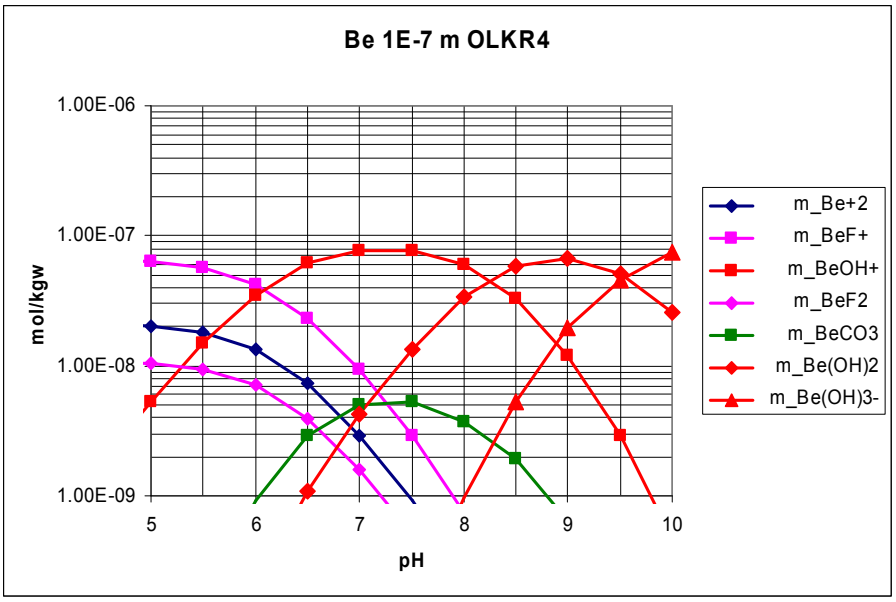

Figure Be-5. *Speciation of Be in brackish KR4_81_1 groundwater.*

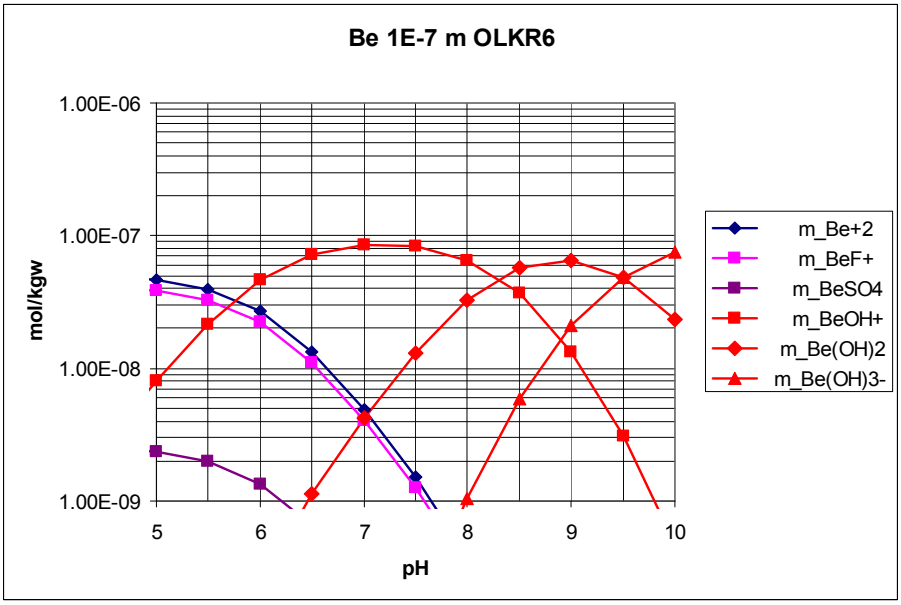

Figure Be-6*. Speciation of Be in brackish KR6_ 135_8 groundwater.*

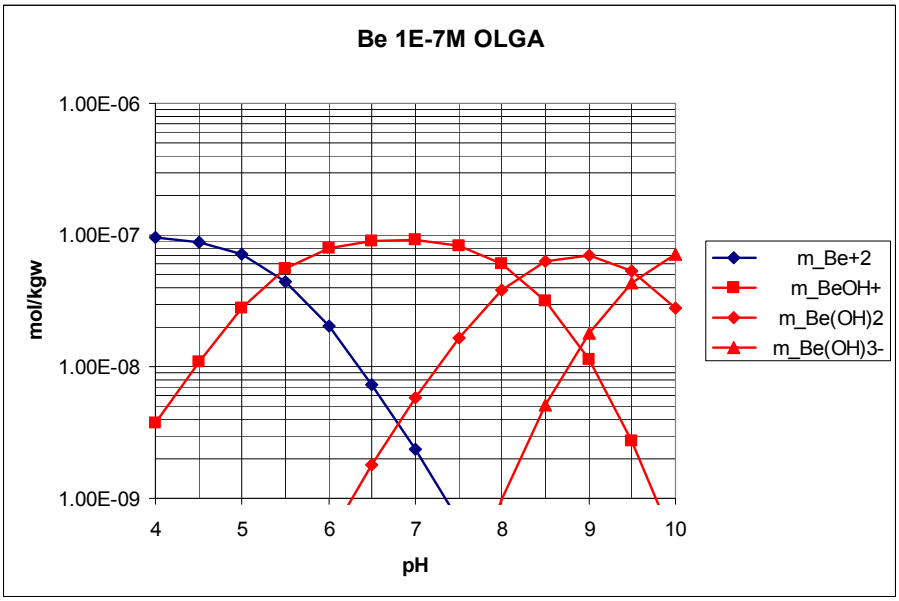

Figure Be-7. *Speciation of Be in glacial OLGA meltwater.*

9.2 Sorption on rocks

9.2.1 Source data

Sorption on biotite and albite as a function of pH in about 0.05 M NaCl solution was determined by Aldahan et al. (1999). The starting Be concentration in their sorption experiments was 0.49 mg/L. Compared to calculated solubility in OLGA water, this exceeds the solubility of $Be(OH)_2$(am) at pH 5.5 and higher, and this was also noticed by Aldahan et al. (1999). High increase of sorption coincided with the pH where the initial solution became oversaturated in respect to $Be(OH)_2$ solids, and probably $Be(OH)_2$(am) precipitated in solutions at pH 5 and higher. In Aldahan et al.(1999), K_d values corrected for this issue are given. The K_d values of biotite (BET/N_2 = 7.9 m^2/g) were anyhow higher than for albite (BET/N_2 = 0.07 m^2/g). Higher sorption to biotite with larger surface area than on albite suggests that sorption also, and not only precipitation, affected the removal of Be from the solution at pH 5 and higher.

Figure Be-8 is from You et al. (1989) from a study of partition of Be between soil and water. In this work, a carrier-free Be-7 isotope ($t_{1/2}$=53 d) was used and the increase of Be concentration due to the tracer was smaller than $2 \cdot 10^{-10}$ M. The K_d values in Figure Be-8 for kaolinite, illite and river mud in fresh river water are in good agreement with the proportion of cationic and neutral Be-hydroxo species of the total Be. Sorption at about pH 8 on illite in the river water and sea water was the same (log K_d= 5.25 mL/g). For montmorillonite, the sorption was less (log K_d= 4.75 mL/g) in sea water (salinity 3.36%) than in the fresh river water (log K_d= 5.25 mL/g). Sorption on illite in natural Taiwan seawater and synthetic seawater was the same (log K_d= 5.5 mL/g). This was interpreted to imply that dissolved organics in the sea water had little effect on K_d.

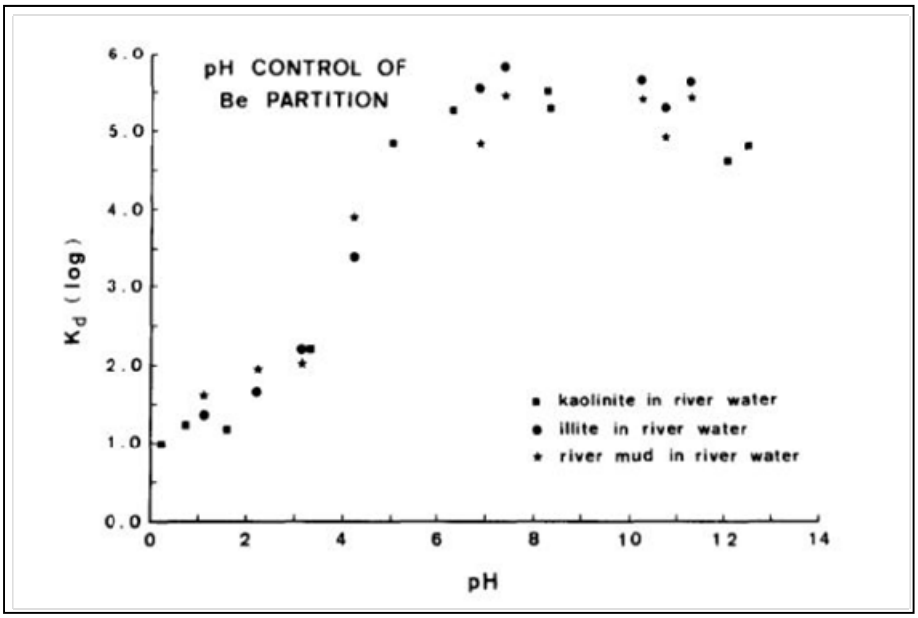

Figure Be-8. *The pH dependence of K_d values (unit of K_d equals to mL/g) of Be in river water for kaolinite, illite and river mud (You et al. 1989).*

Sorption of Be on suspended solids and sediments in environmental waters is high. Decrease of K_d values with increasing solid-to-solution ratio has been reported in many studies on distribution of Be in natural waters between suspended solids and water. This has been explained to be probably due to low solubility of Be in natural waters. Typical K_d values have ranged from 10^2 to 10^3 m^3/kg (Willenbring & von Blanckenburg 2010).

9.2.2 Best estimate K_d values

The speciation of Be in the reference waters and groundwaters indicate that hydroxo complexes are the main species in all waters.

Very limited data were given in the source sorption data for the properties of the rock minerals biotite and albite. The clays in You et al. (1989) were supplied by Ward´s Natural Science Establishment. Kaolinite and illite from Ward´s are mostly American Petroleum Institute (API) clays. CEC and surface areas of API clays were reported by Kemper & Quirk (1972). The CEC and BET/N_2 surface area of API kaolinite (API, Mesa Alta, New Mexico) were reported to be 50 meq/kg and 15 m^2/g. The CEC and BET/N_2 surface area of API35 Fithian illite (Fithian, Illinois) were 220 meq/kg and 100 m^2/g.

Known properties of the named solids must be used for conversion of sorption values between the solids. The K_d values for kaolinite and illite in Figure Be-8 are scattered and the possible impact of larger CEC and BET/N_2 values of illite than of kaolinite to sorption is overwhelmed by the scatter of the K_d values. The speciation of Be implies that cation exchange most probably is not the determining sorption mechanism at pH 4 and higher. However, the CEC values have also been used as the measure for sorption site concentration of clays for elements sorbing by surface complexation (Bradbury & Baeyens 2003). In the conversion of K_d values of the clays to K_d on rocks, the authors

rely more on the CEC of the API illite. The reported CEC (Kemper & Quirk 1972) is in good agreement with the CEC of other illites referred in this report. The BET/N_2 surface areas are very variable for illites (Cerato 2001). The CEC or BET/N_2 values of the clays are not given in You et al. (1989). For the biotite in Aldahan et al. (1999), only the surface area is given. Here the authors assume that the CEC for the biotite was 15 meq/kg (the same as in the Olkiluoto biotite). A CEC of 17 meq/g for Na was also reported for finely ground (BET/N_2, 7 m^2/g) biotite by Allard et al. (1983). For the API illite, we use a CEC value of 220 meq/kg (Cerato 2001). The ratio of the CEC values of illite and biotite (0.07) is about the same as the ratio (0.08) of K_d values at pH 4 for biotite (0.13 m^3/kg) and illite (1.6 m^3/kg) when no solubility limitation of Be was expected in Aldahan et al. (1999) and in You et al. (1989). This ratio (0.07) was used for the derivation of R_d values of Be from data in You et al. (1989) to Olkiluoto biotite (Table Be-1). The K_d values for the rocks in Tables Be-2 – Be-5 were derived from the R_d values for biotite by using the proportions of micaceous minerals+hornblende in the rocks.

The K_d values in Table Be-1 can be compared with K_d values for other hydrolysing cations. The first hydrolysis constant of Be is near to that of europium. According to the LFER (Linear Free Energy Relationship), this suggests that R_d values for sorption of hydroxo complexes of Be are near to that of Eu and higher than for di-valent transition metals, like nickel (Chapter 11). The best estimate K_d values of Eu for the rocks (see Americium, Chapter 19) are very near to the values for Be in Tables Be-2 – Be-5. Only the K_d value for glacial water OLGA is lower for Eu.

Table Be-1. *Source data K_d values of Be to illite (You et al. 1989) and values calculated to the Olkiluoto biotite in the reference waters and at pH 10. KR4 = KR4_81_1, KR6 = KR6_135_8.*

Water	pH	illite	illite	biotite
		log K_d mL/g	K_d m^3/kg	R_d m^3/kg
OLGA	5.8	4.7	5.0E+01	3.5E+00
OLSO	7.2	5.2	1.8E+02	1.2E+01
KR4	7.4	5.2	1.8E+02	1.2E+01
OLBA	7.6	5.2	1.8E+02	1.2E+01
KR6	7.8	5.2	1.8E+02	1.2E+01
OLSR	8.3	5.2	1.8E+02	1.2E+01
ALLMR	8.8	5.2	1.8E+02	1.2E+01
All waters	10.0	5.2	1.8E+02	1.2E+01

Table Be-2. *The best estimate K_d (m^3/kg) values of beryllium for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**9.2E-01**	**9.2E-01**	**3.2E+00**	**3.2E+00**	**3.2E+00**	**3.2E+00**	**3.2E+00**
10	3.2E+00	3.2E+00	3.2E+00	3.2E+00	3.2E+00	3.2E+00	3.2E+00

Table Be-3. *The best estimate K_d (m^3/kg) values of beryllium for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.4E-01**	**4.4E-01**	**1.5E+00**	**1.5E+00**	**1.5E+00**	**1.5E+00**	**1.5E+00**
10	1.5E+00	1.5E+00	1.5E+00	1.5E+00	1.5E+00	1.5E+00	1.5E+00

Table Be-4. *The best estimate K_d (m^3/kg) values of beryllium for T series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.0E-01**	**4.0E-01**	**1.4E+00**	**1.4E+00**	**1.4E+00**	**1.4E+00**	**1.4E+00**
10	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.4E+00

Table Be-5. *The best estimate K_d (m^3/kg) values of beryllium for pegmatite granite PGR at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.9E-01**	**1.9E-01**	**6.4E-01**	**6.4E-01**	**6.4E-01**	**6.4E-01**	**6.4E-01**
10	6.4E-01	6.4E-01	6.4E-01	6.4E-01	6.4E-01	6.4E-01	6.4E-01

9.2.3 Lower limit K_d values

Sorption data to beryllium on well-defined clays and rock minerals are scarce. In contrast to high sorption on clays in You et al. (1989), Ramesh et al. (2002) report R_d values of about $2 \cdot 10^{-2}$ m^3/kg to sorption on bentonite. Even when the initial Be-concentration ($3 \cdot 10^{-3}$ M) in the experiments in Ramesh et al. (2002) exceeded the calculated solubility of Be at the pH of the groundwaters, this low sorption is taken into account by noting that the lower limit sorption is estimated by using Ni(II) as an analogue to Be(II). The hydrolysis of beryllium is stronger than of nickel, but this

difference in speciation is conservatively neglected and the lower limit K_d values for Ni are proposed as the lower limit values for Be. The lower limit K_d values for Be are presented in Tables Be-6 – Be-9.

Table Be-6. *The lower limit K_d values (m^3/kg) of beryllium for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-04**	**7.5E-04**	**1.5E-01**	**5.5E-03**	**3.0E-02**	**7.5E-03**	**3.5E-03**
10	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01

Table Be-7. *The lower limit K_d values (m^3/kg) of beryllium for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.8E-04**	**3.8E-04**	**7.5E-02**	**2.8E-03**	**1.5E-02**	**3.8E-03**	**1.8E-03**
10	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01

Table Be-8. *The lower limit K_d values (m^3/kg) of beryllium for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.3E-04**	**3.3E-04**	**6.5E-02**	**3.5E-03**	**1.3E-02**	**4.0E-03**	**1.5E-03**
10	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01

Table Be-9. *The lower limit K_d values (m^3/kg) of beryllium for pegmatic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.2E-05**	**5.2E-05**	**1.0E-02**	**4.0E-04**	**7.0E-03**	**6.0E-04**	**2.4E-04**
10	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02

9.3 Sorption on clays

9.3.1 Source data

Kaolinite and illite

Source R_d values for kaolinite and illite were taken from Figure Be-8 (You et al. 1989) at the pH of the reference waters. The same values were selected to kaolinite and illite (Table Be-1).

9.3.2 Best estimate K_d values

The R_d values from Figure Be-8 are proposed as the best estimate K_d values for kaolinite and are given in Table Be-10. The best estimate K_d values for illite are presented in Table Be-11.

Kaolinite

***Table Be-10**. The best estimate K_d (m^3/kg) values of beryllium for kaolinite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E+01**	**5.0E+01**	**1.8E+02**	**1.8E+02**	**1.8E+02**	**1.8E+02**	**1.8E+02**
10	1.8E+02	1.8E+02	1.8E+02	1.8E+02	1.8E+02	1.8E+02	1.8E+02

Illite

***Table Be-11**. The best estimate K_d (m^3/kg) values of beryllium for illite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E+01**	**5.0E+01**	**1.8E+02**	**1.8E+02**	**1.8E+02**	**1.8E+02**	**1.8E+02**
10	1.8E+02	1.8E+02	1.8E+02	1.8E+02	1.8E+02	1.8E+02	1.8E+02

9.3.3 Lower limit K_d values

For the same reason as for the rocks, the K_d values of Ni(II), as an analogue to Be(II) are proposed for the lower limit K_d values of Be for kaolinite and illite. Because this is a very conservative choice, no additional uncertainty factors are used.

Table Be-12. *The lower limit K_d (m^3/kg) values of beryllium for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**9.1E-02**	**9.1E-02**	**5.9E-01**	**6.5E-02**	**5.4E-01**	**1.0E-01**	**3.3E-02**
10	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.3E+00	1.4E+00

Table Be-13. *The lower limit K_d (m^3/kg) values of beryllium for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.7E-01**	**4.7E-01**	**1.1E+00**	**6.0E-01**	**8.5E-01**	**5.4E-01**	**6.3E-01**
10	1.1E+00	1.1E+00	1.4E+00	6.6E-01	9.0E-01	5.9E-01	6.6E-01

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10 STRONTIUM AND RADIUM

10.1 Speciation

Strontium and radium are alkaline earth metals and are present in all waters, mainly as divalent cations. The other species in the waters are sulphate, carbonato and chloride complexes. Their proportion is, however, lower than 10 % in all waters.

10.2 Sorption on rocks

10.2.1 Source data

The main sorption mechanism of strontium for silicate minerals in groundwater is cation exchange. The R_d values of Sr and Ra thus decrease with increase in ionic strength and increase with pH. The ions competing with Sr^{2+} and Ra^{2+} in sorption by cation exchange are Ca^{2+} and Na^{+}, which are the main cations in groundwaters. In saline waters, the competition in sorption of Ra is mainly by Sr^{2+} and Ba^{2+}. In the Olkiluoto groundwaters, the concentration (mg/L) of barium (Ba), the alkaline earth cation most near to Ra, is about $1 \cdot 10^{-4}$ times that of Ca, and the concentration of Sr (mg/L) is about 1 % of Ca (Hellä et al. 2014).

Especially in high ionic strength, high pH solutions, the contribution of surface complexation to sorption may be important, but it is low in the groundwaters.

The main reference in the evaluation of sorption is the work on sorption of the alkaline earth elements, Sr, Ba and Ra, on crushed Olkiluoto, Romuvaara and Kivetty rocks by Kulmala & Hakanen (1995). Sorption was determined using the batch method. Sorption on polished thin section samples indicated the preference of sorption to biotite, other micas and hornblende. Sorption isotherms were determined to < 0.1 mm crushed Olkiluoto mica gneiss, tonalite from Romuvaara and granite from Kivetty in brackish/saline OLKR5 water and low salinity KiKR4 water. R_d values at added tracer concentrations of Sr, Ba and Ra in the waters were determined to < 2 mm crushed rocks.

In Kulmala & Hakanen (1995), the R_d values of Sr, Ba and Ra were the highest for the OLKR5 Olkiluoto mica gneiss, as also was the biotite content of the rocks studied. In the experiments, the R_d values were almost the same for different solid-to-solution ratios. This indicates that the removal of the tracers from solution was due to sorption. This is in accordance with the fact that the PHREEQC calculations did not show any oversaturation of the waters by Sr, Ba and Ra carbonates or sulphates.

R_d values of Sr, Ba and Ra for <0.1 mm grain size rocks in saline and fresh groundwaters are in agreement with the so-called direct Hofmeister series for alkaline earth cations (Kulmala & Hakanen 1995). Ba and Ra indicated higher sorption than Sr on the rocks (Figures Sr-1 – Sr-3).

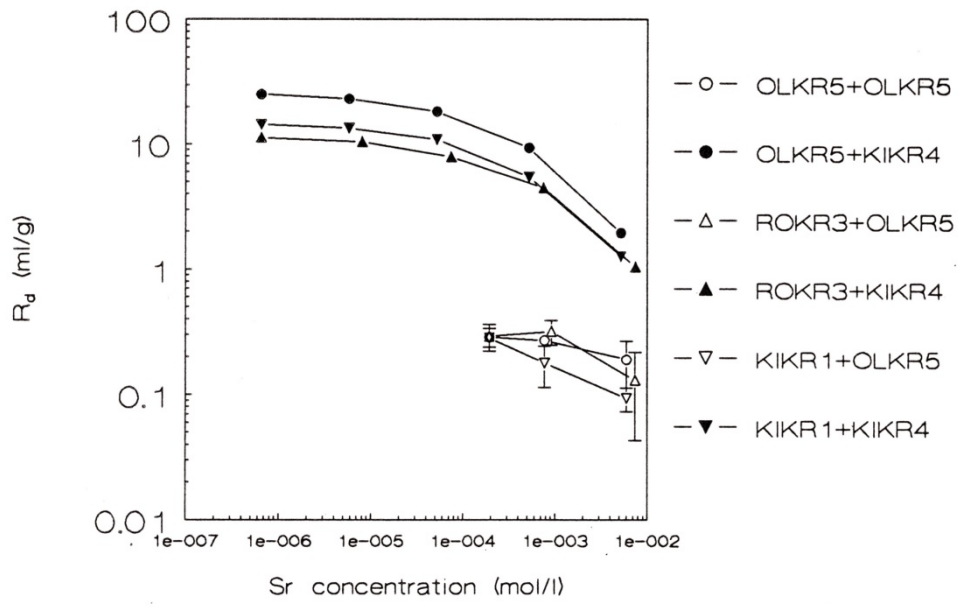

***Figure Sr-1**. Sorption isotherms (R_d ml/g) of Sr for < 0.1 mm grain size OLKR5 mica gneiss, RoKR3 tonalite and KiKR1 granite in OLKR5 (saline) and KiKR4 (fresh) groundwaters. The lowest Sr concentration corresponds to that in the referred groundwater (Kulmala & Hakanen 1995).*

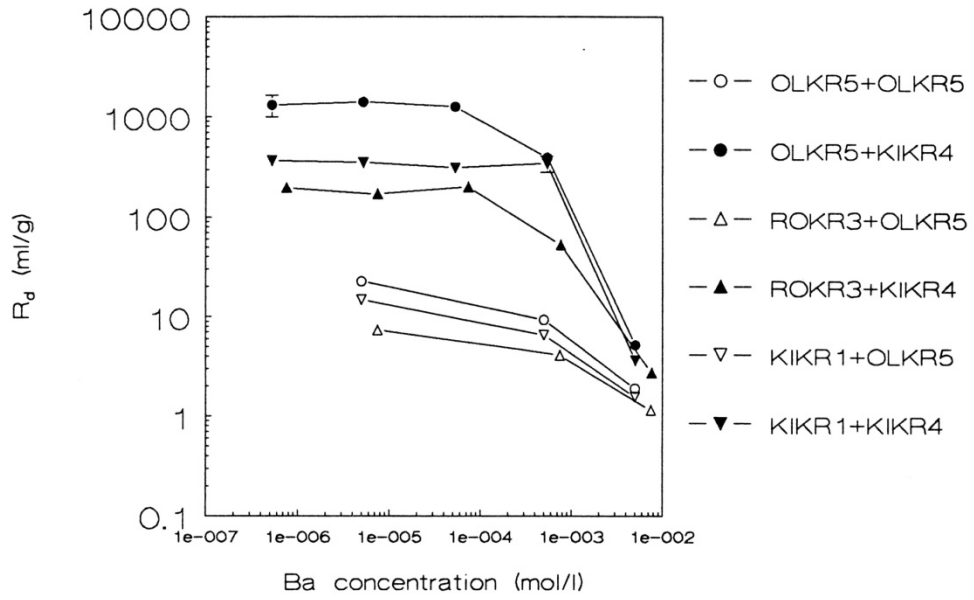

***Figure Sr-2.** Sorption isotherms (R_d ml/g) of Ba for < 0.1 mm grain size OLKR5 mica gneiss, RoKR3 tonalite and KiKR1 granite in OLKR5 (saline) and KiKR4 (fresh) groundwaters. The lowest Ba concentration in OLKR5 corresponds to the determination limit of Ba in saline groundwaters (Kulmala & Hakanen 1995).*

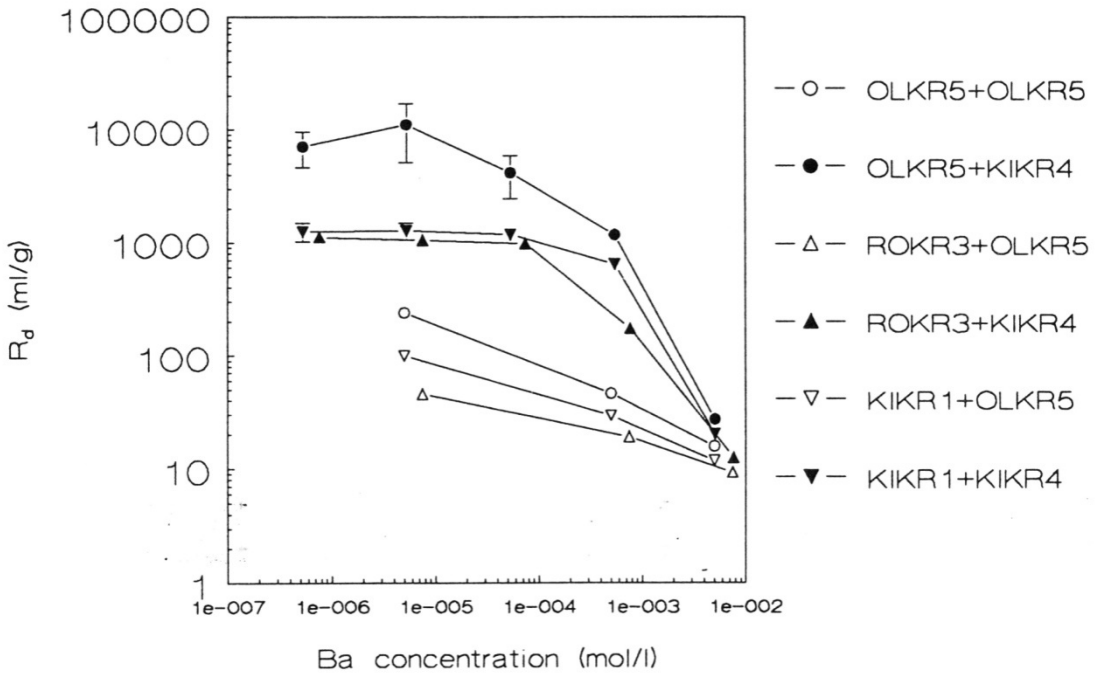

Figure Sr-3. *R_d values (ml/g) of Ra ($2.7 \cdot 10^{-10}$ M) for < 0.1 mm grain size OLKR5 mica gneiss, RoKR3 tonalite and KiKR1 granite in OLKR5 (saline) and KiKR4 (fresh) groundwaters using Ba as carrier (Kulmala & Hakanen 1995).*

Sorption of Sr on the OLKR5 mica gneiss is mainly focused on biotite. Sorption on quartz and feldspars is low, as determined for pure minerals. The surface sorption distribution value of Sr on quartz was $3 \cdot 10^{-6}$ m^3/m^2: for potassium feldspar and plagioclase it was (1.3 - 1.6) $\cdot 10^{-4}$ m^3/m^2 and for biotite $11 \cdot 10^{-4}$ m^3/m^2 (Pinnioja et al. 1986). In the mica gneiss, the proportions of biotite, quartz and feldspar+plagioclase were 22 %, 36 % and 35 % respectively. From the assumption that the surface area of a mineral in a crushed rock sample is proportional to its weight proportion, it follows that over 90 % of Sr is sorbed on biotite.

The sorption mechanism of radium on silicate minerals in the groundwaters is the same as that of Sr, and sorption of Ra is also taken to be over 90 % on biotite. Accessibility of biotite for the sorption of alkaline earth cations is high, as shown in diffusion experiments with Sr (Suksi et al. 1987). These findings allow us to calculate K_d values for the reference rocks by using the biotite concentrations for the conversion of R_d values to the reference rocks.

10.2.2 Calculation of K_d values for the reference rocks

K_d values of Sr, Ba and Ra for the rock types and groundwaters in Kulmala & Hakanen (1995) were calculated from R_d values for the < 2 mm size crushed OLKR5 mica gneiss (Table 8 in Kulmala & Hakanen 1995).

It is assumed that sorption occurs on biotite only and that the amount of sorption sites accessible to alkaline earth cations corresponds to the biotite CEC of 15 µmeq/g in the

OLKR5 mica gneiss, T-MGN T-series mica gneiss, T-TGG T-series tonalite granodiorite granite gneiss and PGR pegmatitic granite and 7.5 µeq/g in P-TGG P-series tonalite granodiorite granite gneiss, as suggested by sorption of Cs on intact rocks in electromigration experiments.

The K_d values of Sr, Ba and Ra to T-MGN mica gneiss were calculated from the R_d values in Table Sr-1 using the ratio of biotite concentration in T-MGN (21.2%) to the OLKR5 mica gneiss (21.0 %) for the rock to rock conversion, and using the estimation above that 90 % of the Sr, Ba or Ra is sorbed on biotite. The K_d values for the other rocks are related to the K_d in T-MGN, using the ratio of accessible CEC in the biotites of the rock as conversion factors. The K_d values for the rocks in OLKR5 water and KiKR4 water are given in Table Sr-2.

In Kulmala & Hakanen (1995), sorption of Sr, Ba and Ra on KiKR4 granite thin sections was also studied using Na, Ca and Cs added waters. In KiKR4 water, Na up to 10^4 times the Sr concentration only marginally affected sorption of Sr or Ba.

For the ionic composition of OLGA, the K_d value is estimated to be much higher than in the low salinity KiKR4 water. However, so as not to overestimate sorption of Sr, the R_d values in KiKR4 are proposed for a solution having the ionic composition of OLGA. The decrease of sorption with decrease of pH to 6 from neutral pH is estimated as being small.

The ratio of R_d values of Sr in KiKR4 water to OLKR5 water has about the same ratio as the Ca-concentration and ionic strengths in the waters. The Ca concentration of fresh ALLMO and ALLMR reference waters is nearly the same as that of fresh KiKR4 water. In KiKR4 water, Sr concentration (mg/L) is less than 1 % of Ca concentration, the average value in the Olkiluoto groundwaters. The ionic strength of the KiKR4 water is about one third of that of ALLMO. The authors conclude that the K_d values of Sr in ALLMR are estimated to be one third of the values in KiKR4 groundwater.

Table Sr-1. *R_d values (m^3/kg) of Sr, Ba and Ra for < 2 mm grain size OLKR5 mica gneiss in brackish/saline OLKR5 water and low salinity KiKR4 water (Kulmala & Hakanen 1995). Only the radioactive tracers (Sr-85, Ba-133m, Ra-226) were added to the groundwaters. The ratio of the mean R_d values, Ca-concentrations (M) and ionic strengths (IS) are indicated. For Sr, the ratio of the higher R_d values is given in parenthesis. The Sr and Ba concentrations in the waters are given.*

	OLKR5 *	KiKR4 **	KI/OL	KI/OL	KI/OL
	R_d	R_d	R_d/R_d	Ca/Ca	IS/IS
Sr	2.60E-5 – 1.00E-4	1.73E-2 – 1.81E-2	280 (180)	220	169
Ba	5.72E-3 – 6.16E-3	4.72E-1 – 5.19E-1	83	220	169
Ra	5.16E-2 – 5.84E-2	3.92E-1 – 5.89E-1	89	220	169

* Sr $1.4 \cdot 10^{-4}$ M, Ba < $1.4 \cdot 10^{-6}$ M, ** Sr $6.0 \cdot 10^{-7}$ M, Ba < $1.2 \cdot 10^{-6}$ M

Table Sr-2. *K_d values of Sr, Ba and Ra for the reference rocks in saline OLKR5 water and fresh KiKR4 water using experimental minimum and maximum R_d values for the elements in OLKR5 mica gneiss. Rocks T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

K_d values for the reference rocks in OLKR5 water					
		T-MGN	P-TGG	T-TGG	PGR
Sr	min	2.3E-05	1.2E-05	9.1E-06	1.0E-06
	max	9.0E-04	4.7E-05	3.5E-05	3.9E-06
Ba	min	5.2E-03	2.7E-03	2.0E-03	2.2E-04
	max	5.5E-03	2.8E-03	2.2E-03	2.4E-04
Ra	min	4.6E-02	2.4E-02	1.8E-02	2.0E-03
	max	5.3E-02	2.7E-02	2.0E-02	2.3E-03
K_d values for the reference rocks in KiKR4 water					
		T-MGN	P-TGG	T-TGG	PGR
Sr	min	1.6E-02	8.0E-03	6.1E-03	6.7E-04
	max	1.6E-02	8.0E-03	6.4E-03	7.0E-04
Ba	min	4.3E-01	2.2E-01	1.7E-01	1.8E-02
	max	4.7E-01	2.4E-01	1.8E-01	2.0E-02
Ra	min	3.5E-01	1.8E-01	1.4E-01	1.5E-02
	max	5.3E-01	2.8E-01	2.1E-01	2.3E-02

For brackish OLBA reference water, the Ca concentration is ten times higher than in KiKR4. This suggests that the K_d of Sr in OLBA is about $1.8 \cdot 10^{-3}$ m^3/kg to T-MGN. On the other hand, the ratio of Sr concentration in OLKR5 to OLBA (KR6_135_8) is 17/1.7. The K_d values in OLBA can thus be estimated to be ($7 \cdot 10^{-4}$ m^3/kg to T-MGN), 10 times higher than in OLKR5. The OLBA water was to simulate the KR6_135_8 groundwater. The ratio of calcium concentration of this water to Ca in OLKR5 is 1/2.8. The K_d value of Sr in OLBA is estimated to be 3 times that in OLKR5. Using this ratio gives lower K_d values than using the Sr concentration ratio and is proposed as the best estimate in order not to overestimate sorption of Sr.

The Ca and Sr concentration of OLSR is 1.8 times that of OLKR5. The K_d value of Sr in OLSR is suggested to be the one half of the values in OLKR5 water.

The ratio of Ca concentration in saline KR20_465_1 water to OLKR5 is 0.6. It is estimated that the K_d of Sr in KR20_465_1 is 1.5 times higher than that in OLKR5.

For Ra and Ba, the R_d values are much higher than for Sr, and sorption of Ra and Ba was less reduced with increasing Ca-concentration or ionic strength of the waters. For the sake of conservatism, the same conversions used for Sr are used in the calculation of K_d values in the waters.

The K_d of Ra in OLGA is taken to be the same as in the KiKR4 water for the same reason as the K_d for Sr. The ionic strength in fresh ALLMR is three times that in KiKR4. It is here assumed that the barium concentration in ALLMR type natural water

is also three times that in KiKR4 water. It follows that the K_d of Ra in ALLMR is assumed to be one third of the value in KiKR4 water.

For the same reason as for Sr, the K_d values of Ra are estimated to be 3 times that in OLKR5. Using this ratio gives lower K_d values than using the Sr concentration ratio, and is used in order not to overestimate sorption of Ra.

Based on the same reasoning as for Sr, it is estimated that the K_d of Ra in the KR20_465_1 water is 1.5 times higher than that in OLKR5.

The Ca and Sr concentration ratio in OLSR to OLKR5 water is 1.8, and the K_d of Ra in OLSR is suggested to be half of the value in OLKR5 water.

pH dependence of K_d of Sr

No reference for the pH-dependence of sorption of Sr or Ra on relevant rock types is available. Carroll et al. (2008) determined high pH dependence between pH 6 and pH 10 in sorption of Sr on amorphous silica (BET/N_2 surface area 227 m^2/g) in NaCl solutions. The highest sorption was for the lowest Sr concentration in the lowest (0.005 M) NaCl concentration. The R_d (m^3/kg) values were $4 \cdot 10^{-3}$, $13 \cdot 10^{-3}$, $80 \cdot 10^{-3}$ and $980 \cdot 10^{-3}$ at pH 6, 7, 8 and 9 respectively. Silica has no permanent charge and the sorption edge was modelled using the surface complexation approach. Conversion of the R_d values to the crushed reference rocks using BET/N_2 surface area ratio as the conversion factor gives R_d values $1.5 \cdot 10^{-5}$, $5 \cdot 10^{-5}$, $3 \cdot 10^{-4}$ and $4 \cdot 10^{-3}$ m^3/kg for pH 6, 7, 8 and 9 respectively. This suggests that surface complexation may increase sorption of Sr, especially on PGR pegmatitic granite, to which sorption by cation exchange is the lowest of the rocks. For the other rocks, the impact of surface complexation is less. In the other reference waters, the impact of high pH on sorption is smaller. If calcite is precipitated at higher pH, it will enhance the removal of Sr and Ra from solution.

Nikula (1982) determined R_d values of Sr for a Baltic clay at pH 3 to pH 9. The R_d values increased/decreased by about 8% per pH-unit as compared to the R_d at pH 7.

Owing to the fact that the effect of pH on sorption is minor, no correction for pH is made to the K_d values of Sr.

pH dependence of K_d of Ra

Tachi et al. (2001) determined R_d values of radium for Kunigel bentonite and purified smectite at pH 7 to 11. The R_d values for the purified smectite at pH 7 and 8 were about the same. For pH 9 and pH 10, the R_d values were higher than at pH 8. For the Kunigel bentonite containing both calcite (2.5%) and dolomite (2-3.8%), the sorption of Ra was influenced by dissolution and precipitation of calcite and other impurities in the bentonite, and no such increase with pH was found. Due to uncertainties, no correction for pH is made to the K_d values of Ra for the rocks.

10.2.3 Best estimate K_d values

The amount of biotite in the T-series mica gneiss T-MGN and P-series tonalite granodiorite granite gneiss P-TGG is the same as in the mica gneiss OLKR5. The accessible CEC of the biotites (15 μmeq/g) in T-MGN and OLKR5 mica gneisses and T-TGG tonalite granodiorite granite gneiss is estimated to be the same. In P-TGG it is estimated to be half of that in OLKR5. For the pegmatitic granite PGR, K_d values were calculated using only the biotite concentration, and using the sum of biotite and muscovite as the sorbing minerals. The K_d values of Sr are given in Tables Sr-3 – Sr-6 and K_d values of Ra are given in Tables Sr-7 – Sr-10.

Table Sr-3. *Best estimate K_d values (m^3/kg) of Sr for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.6E-02**	**1.6E-02**	**5.4E-03**	**5.4E-03**	**6.0E-04**	**1.2E-05**	**1.2E-05**	**2.0E-03**	**3.0E-05**
10	1.6E-02	1.6E-02	5.4E-03	5.4E-03	6.0E-04	1.2E-05	1.2E-05	2.0E-03	3.0E-05

Table Sr-4. *Best estimate K_d values (m^3/kg) of Sr for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**8.0E-03**	**8.0E-03**	**2.6E-03**	**2.6E-03**	**3.0E-04**	**6.0E-06**	**6.0E-06**	**1.0E-03**	**1.5E-05**
10	8.0E-03	8.0E-03	2.6E-03	2.6E-03	3.0E-04	6.0E-06	6.0E-06	1.0E-03	1.5E-05

Table Sr-5. *Best estimate K_d values (m^3/kg) of Sr for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**6.1E-03**	**6.1E-03**	**2.0E-03**	**2.0E-03**	**2.0E-04**	**4.6E-06**	**4.6E-06**	**1.0E-03**	**1.0E-05**
10	6.1E-03	6.1E-03	2.0E-03	2.0E-03	2.0E-04	4.6E-06	4.6E-06	1.0E-03	1.0E-05

Table Sr-6. *Best estimate K_d values (m^3/kg) of Sr for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**6.7E-04**	**6.7E-04**	**2.2E-04**	**2.2E-04**	**2.0E-05**	**5.0E-07**	**5.0E-07**	**1.0E-04**	**1.0E-06**
10	6.7E-04	6.7E-04	2.2E-04	2.2E-04	2.0E-05	5.0E-07	5.0E-07	1.0E-04	1.0E-06

Table Sr-7. *Best estimate K_d values (m^3/kg) of Ra for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.5E-01**	**3.5E-01**	**1.2E-01**	**1.2E-01**	**6.0E-02**	**2.3E-02**	**2.3E-02**	**1.0E-01**	**4.0E-02**
10	3.5E-01	3.5E-01	1.2E-01	1.2E-01	6.0E-02	2.3E-02	2.3E-02	1.0E-01	4.0E-02

Table Sr-8. *Best estimate K_d values (m^3/kg) of Ra for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.7E-01**	**1.7E-01**	**6.0E-02**	**6.0E-02**	**3.0E-02**	**1.2E-02**	**1.2E-02**	**5.0E-02**	**2.0E-02**
10	1.7E-02	1.7E-02	6.0E-02	6.0E-02	3.0E-02	1.2E-02	1.2E-02	5.0E-02	2.0E-02

Table Sr9. *Best estimate K_d values (m^3/kg) of Ra for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.4E-01**	**1.4E-01**	**4.6E-02**	**4.6E-02**	**3.0E-02**	**9.1E-03**	**9.1E-03**	**4.0E-02**	**4.0E-02**
10	1.4E-01	1.4E-01	4.6E-02	4.6E-02	3.0E-02	9.1E-03	9.1E-03	4.0E-02	4.0E-02

Table Sr-10. *Best estimate K_d values (m^3/kg) of Ra for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.5E-02**	**1.5E-02**	**5.0E-03**	**5.0E-03**	**3.0E-03**	**1.1E-03**	**1.1E-03**	**4.0E-03**	**2.0E-03**
10	1.5E-02	1.5E-02	5.0E-03	5.0E-03	3.0E-03	1.1E-03	1.1E-03	4.0E-03	2.0E-03

10.2.4 Lower limit K_d values

Mineralogical uncertainties due to biotite abundances are about 30 % for T-MGN T-series mica gneiss and P-TGG P-series tonalite granodiorite granite gneiss, 100 % for T-TGG T-series tonalite granodiorite granite gneiss and 200 % for PGR pegmatitic granite. For OLKR5 mica gneiss, the uncertainty of the biotite content is taken to be the same as for T-MGN and P-TGG. Accessibility of the biotite sorption sites for alkaline earth cations, as compared to the accessibility in the < 2 mm crushed OLKR5 mica gneiss, is assumed to be the same for T-MGN, T-TGG and PGR but in the P-TGG it is assumed to be 50 % of that in the OLKR5 mica gneiss.

Chemical uncertainties arise both from the ionic composition of the waters and especially the Ra and Ba concentration that was lower than the determination limit (0.2 mg/L) in OLKR5 water. The highest Ba concentrations in the Olkiluoto groundwaters have been 3 mg/L ($2.3 \cdot 10^{-6}$ M) (Hellä et al. 2014). For the < 0.1 mm grain size OLKR5 mica gneiss in KiKR4 water, an increase of Ba concentration from $1 \cdot 10^{-6}$ M to $2 \cdot 10^{-5}$ M was followed by a decrease in the R_d value of Ra from 7 m^3/kg to 4 m^3/kg. The natural Ba concentration is assumed not to reduce sorption of Ra from the values measured in Kulmala & Hakanen (1995).

In saline OLSR, the total alkaline earth concentration is more important for sorption of Ra than the Ba concentration. The chemical compositions of the waters are well known and care was taken not to overestimate the best estimate K_d values.

In the calculation of K_d values for the waters from the R_d data in OLKR5, the same selectivity of Sr, Ra and Ca was assumed. This underestimates sorption of Sr and Ra. In addition, so as not to overestimate sorption, the best estimate K_d values were calculated using the lower limit experimental values.

It is difficult to quantitatively estimate the impact of the different uncertainties on the total uncertainty. It is regarded as reasonable that the lower limit values are calculated for the rocks by dividing the best estimate values by uncertainty factors calculated for each rock type (Table Sr-11). The lower limit K_d values of Sr and Ra are shown in Tables Sr-12 – Sr-15 and Sr-16 – Sr-19 respectively.

Table Sr-11. *The uncertainty factors of Sr and Ra for rocks. T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

Reference rock	Factor for random error calculation
T-MGN, P-TGG	20
T-TGG	20*
PGR	50*
*error propagation using the errors in the mica contents and BET/N_2 (surface area) of micas and crushed rock yields unrealistically low correction factor for T-MGN and PGR. Omitting the error in BET/N_2 of crushed rock the factor for T-TGG is 7 and for PGR 43.	

Table Sr-12. *Lower limit K_d values (m^3/kg) of Sr for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**8.0E-04**	**8.0E-04**	**2.7E-04**	**2.7E-04**	**3.0E-05**	**6.0E-07**	**6.0E-07**	**1.0E-04**	**1.5E-06**
10	8.0E-04	8.0E-04	2.7E-04	2.7E-04	3.0E-05	6.0E-07	6.0E-07	1.0E-04	1.5E-06

Table Sr-13. *Lower limit K_d values (m^3/kg) of Sr for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.0E-04**	**4.0E-04**	**1.8E-04**	**1.8E-04**	**1.5E-05**	**3.0E-07**	**3.0E-07**	**5.0E-05**	**7.0E-07**
10	4.0E-04	4.0E-04	1.8E-04	1.8E-04	1.5E-05	3.0E-07	3.0E-07	5.0E-05	7.0E-07

Table Sr-14. *Lower limit K_d values (m^3/kg) of Sr for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.1E-04**	**3.1E-04**	**1.0E-04**	**1.0E-04**	**1.0E-05**	**2.3E-07**	**2.3E-07**	**5.0E-05**	**5.0E-07**
10	3.1E-04	3.1E-04	1.0E-04	1.0E-04	1.0E-05	2.3E-07	2.3E-07	5.0E-05	5.0E-07

Table Sr-15. *Lower limit K_d values (m^3/kg) of Sr for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.3E-05**	**1.3E-05**	**4.4E-06**	**4.4E-06**	**4.0E-07**	**1.0E-08**	**1.0E-08**	**2.0E-06**	**2.0E-08**
10	1.3E-05	1.3E-05	4.4E-06	4.4E-06	4.0E-07	1.0E-08	1.0E-08	2.0E-06	2.0E-08

Table Sr-16. *Lower limit K_d values (m^3/kg) of Ra for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.8E-02**	**1.8E-02**	**6.0E-03**	**6.0E-03**	**3.0E-03**	**1.2E-03**	**1.2E-03**	**5.0E-03**	**2.0E-03**
10	1.8E-02	1.8E-02	6.0E-03	6.0E-03	3.0E-03	1.2E-03	1.2E-03	5.0E-03	2.0E-03

Table Sr-17. *Lower limit K_d values (m^3/kg) of Ra for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**9.0E-03**	**9.0E-03**	**3.0E-03**	**3.0E-03**	**1.5E-03**	**6.0E-04**	**6.0E-04**	**2.5E-03**	**1.0E-03**
10	9.0E-04	9.0E-04	3.0E-03	3.0E-03	1.5E-03	6.0E-04	6.0E-04	2.5E-03	1.0E-03

Table Sr-18. *Lower limit K_d values (m^3/kg) of Ra for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**7.0E-03**	**7.0E-03**	**2.3E-03**	**2.3E-03**	**1.5E-03**	**4.6E-04**	**4.6E-04**	**2.0E-03**	**2.0E-03**
10	7.0E-03	7.0E-03	2.3E-03	2.3E-03	1.5E-03	4.6E-04	4.6E-04	2.0E-03	2.0E-03

Table Sr-19. *Lower limit K_d values (m^3/kg) of Ra for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.0E-04**	**3.0E-04**	**1.0E-04**	**1.0E-04**	**6.0E-05**	**2.2E-05**	**2.2E-05**	**8.0E-05**	**8.0E-04**
10	3.0E-04	3.0E-04	1.0E-04	1.0E-04	6.0E-05	2.2E-05	2.2E-05	8.0E-05	8.0E-04

10.3 Sorption on clays

In the literature, the R_d values of strontium for kaolinite have seldom been reported, but those reported are of the same magnitude, varying between $1.20 \cdot 10^{-2}$ m^3/kg to $7.70 \cdot 10^{-2}$ m^3/kg (Andersson et al. 1983, Ticknor et al. 1991).

10.3.1 Source data

Strontium

Kaolinite

R_d values of Sr for the kaolinite in 0.1 M NaCl were calculated from the R_d values of batch experiments by Sahai et al. (2000). In these experiments, the kaolinite was KGa-1b with BET/N_2 surface area of 11.5 m^2/g and the solid to solution ratio was 39.65 g/L in 0.1 M NaCl solution. The initial Sr concentration was 10^{-3} M. The R_d values were calculated for kaolinite in 0.1 M NaCl as a function of pH (Table Sr-20). In the data of Sahai et al. (2000) the sorption of Sr increases with increasing pH.

R_d values of Sr for kaolinite in the reference waters were calculated from the sorption data of Sahai et al. (2000) and are given in Table Sr-21. A very robust estimation was made that for kaolinite the selectivity in cation exchange is the same as for Ca, Sr and Ra and two times that of Na. The R_d values for Sr are corrected for ionic strength by multiplying the values for 1mM Sr in 0.1 M NaCl by the ratio of Na concentration in the experiment by Sahai et al. (2000), i.e. 100 mM by the cationic charge (CAT) in the reference water.

Sorption of Sr was also calculated from the graph in Jeong (2001, Figure 1) to sorption on Georgia kaolinite. R_d values were calculated from the sorption data for Sr ($1 \cdot 10^{-6}$ M)

in 0.1 to $1 \cdot 10^{-5}$ M NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions at pH 7. R_d values of Sr in the reference waters were calculated for Na- and combined Ca+Mg-concentrations in the waters (Table Sr-22). For the saline water OLSR, R_d was calculated to be higher for the K concentration than for the Na and Ca+Mg-concentrations. The R_d values for Na- and Ca+Mg-concentrations show that the competition in the sorption of Sr by Na and Ca+Mg is about the same in the saline waters, and the R_d values calculated from Na-concentrations and from Ca+Mg-concentrations are within a factor of two for all waters.

Sorption of Sr on kaolinite in Jeong (2001) increases with pH and the increase depends on the background electrolyte. No interpretation for this is given. The data used for the calculation of the R_d values in the groundwaters was determined at pH 7. From pH 7 to pH 6 the change in sorption is not very different in Jeong (2001). The data of Sahai et al. (2000) is too scattered at low pH to draw any conclusions on pH dependency at the pH of the glacial meltwater (5.8). For the sake of conservatism, it is assumed here that the sorption of Sr on kaolinite is the same for all pH values of the waters.

Table Sr-20. *The calculated R_d values (m^3/kg) of 1 mM Sr for kaolinite in 0.1 M NaCl in anoxic conditions (Sahai et al. 2000).*

pH final	S(%)	R_d(m^3/kg)
6.66	0.62	0.000156
7.19	4.5	0.001178
7.18	0.51	0.000128
7.70	4.1	0.001069
8.20	6.2	0.001653
8.38	7.1	0.001911
8.88	8.6	0.002352
9.41	13.9	0.004036
9.78	18.6	0.005713

Table Sr-21. *R_d (m^3/kg) values of Sr (1mM)) for kaolinite at Olkiluoto calculated from the experimental data (Sahai et al. 2000). CAT = cationic charge concentration (mmol) in the reference water. Waters KR6 = KR6_135_8; KR4 = KR4_81_1; KR20 = KR20_465_1.*

water	CAT (mmol)	R_d (m^3/kg)
OLGA	0.07	2.0E-01
OLSR	410	4.0E-04
KR6 (OLBA)	110	1.0E-03
KR4	24	4.0E-03
KR20	191	5.0E-04
ALLMR	3.1	7.0E-02

Table Sr-22. *R_d (m^3/kg) values of Sr for kaolinite calculated from Jeong (2001) for Na and Ca+Mg-concentrations in the waters. Waters KR6 = KR6_135_8; KR4 = KR4_81_1; KR20 = KR20_465_1.*

water	ions	ion conc. C (M)	sorption (%)	R_d (m^3/kg)
OLGA	Na	0.00003	80	0.121
	Ca+Mg	0.00002	65	0.056
OLSR	Na	0.209	10	0.0034
	K	0.00054	55	0.037
	Ca+Mg	0.1023	10	0.0034
KR6	Na	0.0779	17	0.0062
	Ca+Mg	0.02327	10	0.0034
KR4	Na	0.01125	55	0.037
	Ca+Mg	0.00181	30	0.013
KR20	Na	0.12	10	0.0034
	Ca+Mg	0.01921	10	0.0034
ALLMR	Na	0.0013	70	0.070
	Ca+Mg	0.00036	45	0.025

Illite

Sorption of Sr on IMt-1 illite was calculated using the PHREEQC programme. The cation exchange selectivity coefficients for Na/K, Na/Cs and Na/Ca exchange for illite in Bradbury & Baeyens (2000, 2005) were used. The same value of the selectivity coefficient for Na/Sr exchange as for Na/Ca was used. The cation exchange capacity of the IMt-1 illite has been reported to be 170 meq/kg (Missana et al. 2008) and 250 meq/kg (Polusebova & Nir 1999). The CEC used in the calculations was 225 meq/kg, reported for du Puy illite by Baeyens & Bradbury (2004). The proportions of site capacities in Bradbury & Baeyens (2000, 2005) were used. The Sr concentration in the calculations was assumed to be minor compared with the Ca-concentration in the waters. The R_d values were calculated for the Ca concentration in the waters.

The pH dependency of the sorption of Sr on illite under an inert atmosphere in electrolyte solution indicated that the sorption at pH 3-9 is the same (Missana et al. 2008). An increase in sorption at pH higher than 9 is observed, owing to the impact of sorption by surface complexation (Poinssot et al. 1999, Missana et al. 2008). At pH 10 in 0.1 M $NaClO_4$, the sorption was two times that at pH 8 (Missana et al. 2008). However, so as not to overestimate sorption in the groundwaters, we assume that sorption is the same as that calculated using the cation exchange model.

Radium

No data for the sorption of Ra on kaolinite has come to the attention of the authors of this report.

No selectivity coefficients of cation exchange of Ra on illite have come to the attention of the authors. Ames (1983a) gives K_d values of 8-16 m^3/kg of radium in 0.01 M NaCl for illite (CEC 250 meq/kg for Cs, Ames 1983b). The K_d values for Sr calculated for Ca are not larger than the values calculated by Ames (1983a, b). It follows that the use of

the K_d values of Sr for Ra does not overestimate the sorption of Ra, and this is proposed for the sorption of Ra.

10.3.2 Best estimate K_d values

Strontium

Kaolinite

The R_d values of Sr to kaolinite in the reference waters derived from graphs in Jeong (2001) to the Na- and Ca+Mg-concentrations in the groundwaters are given in Table Sr-21. These values are based on better source data than that given in Sahai et al. (2000). The values derived from the data of Sahai et al. (2000) are for high (1mM) Sr concentration and for only one Na-concentration.

The lab-to field conversion factor is unity. So as not to overestimate sorption, the K_d values based on the R_d values calculated for Ca+Mg-concentrations are proposed as the best estimate values. The values are given in Table Sr-23.

The K_d values of Sr are converted using the Na-concentration of the waters. For radium, the same best estimate K_d values as for Sr are proposed (Table Sr-23).

Illite

Sorption of Sr by cation exchange is highly dependent on the salinity of water. Owing to limited data on surface complexation of Sr, the same sorption at pH 10 in the waters is proposed as at the nominal pH of the waters. The best estimate K_d values for illite are given in Table Sr-24.

Table Sr-23. *Best estimate K_d values (m^3/kg) of Sr (1mM)) and Ra for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.* The *K_d values are calculated from the experimental data (Jeong 2001).*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**5.6E-02**	**5.6E-02**	**2.5E-02**	**2.5E-02**	**3.4E-03**	**3.4E-03**	**3.4E-03**	**1.3E-02**	**3.4E-03**
10	6.0E-02	6.0E-02	2.5E-02	2.5E-02	3.4E-03	3.4E-03	3.4E-03	1.3E-02	3.4E-03

Table Sr-24. *Best estimate of K_d values (m^3/kg) of Sr and Ra for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**7.8E+00**	**7.8E+00**	**1.9E-01**	**1.9E-01**	**2.3E-02**	**6.6E-04**	**6.6E-04**	**5.8E-02**	**2.0E-03**
10	7.8E+00	7.8E+00	1.9E-01	1.9E-01	2.3E-02	6.6E-04	6.6E-04	5.8E-02	2.0E-03

Radium

The use of the best estimate K_d values of Sr to Ra does not overestimate the sorption of Ra and is proposed for the sorption of Ra on illite and kaolinite (Tables Sr-23, Sr-24).

10.3.3 Lower limit K_d values

Strontium

The overall uncertainty factor (UF_{tot}) for intact fracture clays at Olkiluoto is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source}*UF_{model}*UF_{CEC}*UF_{spec}*UF_{pH}*UF_{lab\_field} \quad \text{(Sr-1)}$$

The lower limit of the K_d(LL) is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\ (LL) = K_d(BE)/UF_{tot} \quad \text{(Sr-2)}$$

Kaolinite

UF_{source} varies from 2 to 5. The source data for K_d values are solely from graphs in the literature. For Sr, the other alkaline earth metals Ca and Mg have a larger impact on sorption than alkaline ions, especially potassium. The sorption values in the graph in Jeong (2001, Figure 1) for the ion concentrations of the groundwaters and simulants are accurate to the level that an uncertainty factor UF_{source} of 2 covers this uncertainty for the fresh and brackish waters. For the saline waters, the UF_{source} value of 5 is used to cover the uncertainty in reading the graph.

UF_{model} = 1. No sorption model was used for sorption on kaolinite.

UF_{CEC} = 1. The sorption mechanism is ion exchange. The impact of sorption by surface complexation probably increases sorption at pH 10. This impact is not taken into account. Since the source data were for a well-crystallised kaolinite, which sorbs in equal amounts or less compared with the Olkiluoto kaolinite (the degree of crystallinity is unknown), there is no need for a correction factor concerning differences between the source data and reference conditions. However, the CEC for kaolinite is in general not very high and it was considered that the uncertainty is not significant (see Chapter 3).

UF_{spec} = 1.4. The experiments were not performed in the reference waters.

UF_{pH} = 2. No conversion for possible pH dependency of sorption was included in the best estimate values. The uncertainty factor UF_{pH} is taken as suggested by the data of Sahai et al. (2000).

UF_{lab_field} = 2. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 11 to 28.

The uncertainty factors for kaolinite are collected in Table Sr-25. Only those factors which are greater than one are listed.

The lower limit K_d values for kaolinite at Olkiluoto are calculated in Table Sr-26.

Illite

Most of the uncertainty factors for illite are the same as for kaolinite.

UF_{model} = 1. In the sorption model, the selectivity coefficient for Ca/Na exchange was adopted to Sr/Na exchange. The selectivity in sorption by cation exchange of earth alkaline cations on clays is generally found to increase with increase of the non-hydrated radius of the ion (Stumm & Morgan 1996). The calculation thus underestimates sorption of Sr and the use of UF_{model} = 1 is proposed.

UF_{CEC} = 1.3. For illite at Olkiluoto, the R_d values are calculated using the cation exchange model in the PHREEQC program. The uncertainty in the properties of the illite to which the selectivity coefficients were calculated and the Olkiluoto site illite is taken into account in the uncertainty factor UF_{CEC} which was taken to be 1.3, since the CEC of the source data illite and the Olkiluoto illite may be different (see Chapter 3).

UF_{tot} = 15 (2*1.3*2*1.4*2).

The lower limit K_d values for illite at Olkiluoto are calculated in Table Sr-27.

Radium

The use of the best estimate K_d values of strontium to radium does not overestimate the sorption of Ra and was proposed for the sorption of Ra on clays. Likewise, the uncertainty factors of Sr are used for radium (Table Sr-25). The lower limit K_d values for illite and kaolinite are calculated in Tables Sr-26 and Sr-27.

Table Sr-25. *The uncertainty factors (UF) of Sr and Ra for kaolinite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	UF_{source}	UF_{pH}	UF_{spec}	UF_{Lab_field}	UF_{tot}
OLGA	2	2	1.4	2	11
OLGO	2	2	1.4	2	11
ALLMR	2	2	1.4	2	11
ALLMO	2	2	1.4	2	11
OLBA	2	2	1.4	2	11
OLSR	5	2	1.4	2	28
OLSO	5	2	1.4	2	28
KR4	2	2	1.4	2	11
KR20	5	2	1.4	2	28

Table Sr-26. *Lower limit K_d values (m^3/kg) of Sr (1mM) and Ra for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.1E-02**	**1.1E-02**	**1.8E-02**	**1.8E-02**	**3.0E-04**	**3.0E-04**	**3.0E-04**	**1.2E-03**	**3.0E-04**
10	1.1E-02	1.8E-02	1.8E-02	1.8E-02	3.0E-04	3.0E-04	3.0E-04	1.2E-03	3.0E-04

Table Sr-27. *Lower limit K_d values (m^3/kg) of Sr and Ra for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**5.4E-01**	**5.4E-01**	**1.3E-02**	**1.3E-02**	**1.6E-03**	**4.5E-05**	**4.5E-05**	**4.0E-03**	**1.4E-04**
10	5.4E-01	5.4E-01	1.3E-02	1.3E-02	1.6E-03	4.5E-05	4.5E-05	4.0E-03	1.4E-04

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11 NICKEL

11.1 Speciation

Ni is found in the groundwaters in the form of Ni(II). Its concentration in the Olkiluoto groundwaters ranges from < 8 $\cdot 10^{-8}$ M to 1.1 $\cdot 10^{-6}$ M (Hellä et al. 2014). The speciation of nickel was calculated with the PHREEQC programme using the database Thermo_Chimie Version 7b (ANDRA 2009). Speciation of Ni ($1.7 \cdot 10^{-7}$ m) in glacial OLGA, fresh ALLMR, brackish OLBA, saline OLSR, brackish KR4_81_1 and saline KR20_465_1 waters are presented in Figures Ni-1 – Ni-7. The sorbing species are Ni^{2+} ion and the hydroxo complexes $Ni(OH)^{+}$ and $Ni(OH)_2$. The proportion of Ni^{2+} at pH 8 in the water is 77 to 99 %. The lowest proportion of Ni^{2+} at pH 8 is in KR4_81_1 water. The proportion of hydroxo complexes at pH 8 is higher for the fresh low carbonate water and lower for the saline waters. At pH 10, the main species in all waters is $Ni(OH)_2$ varying between 82–88 % of total Ni. The Ni-chlorido and Ni-carbonato complexes are regarded as non-sorbing.

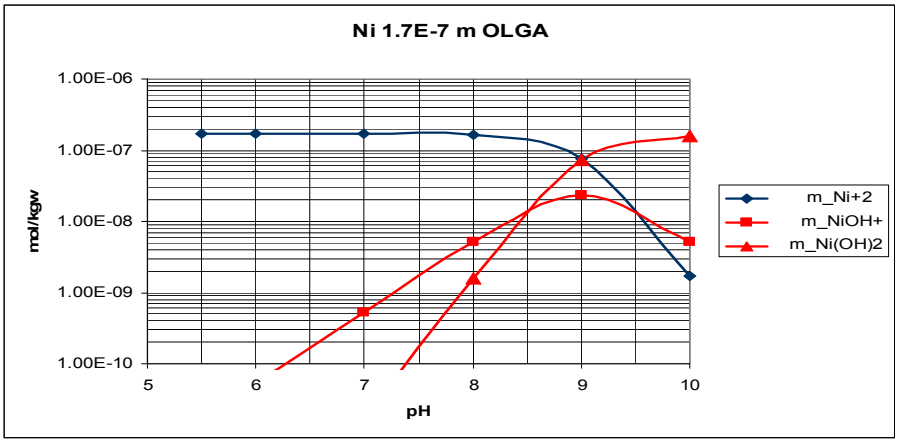

***Figure Ni-1**. Soluble species of Ni in glacial OLGA water.*

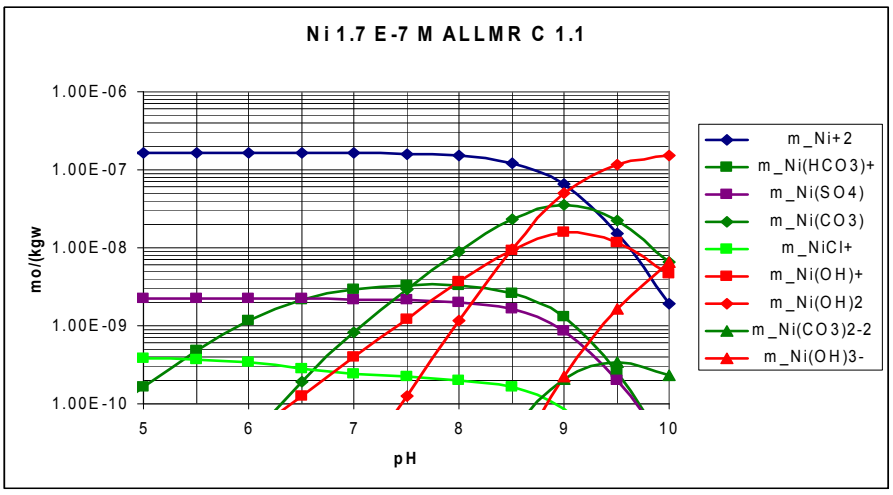

***Figure Ni-2.** Soluble species of Ni in fresh ALLMR water.*

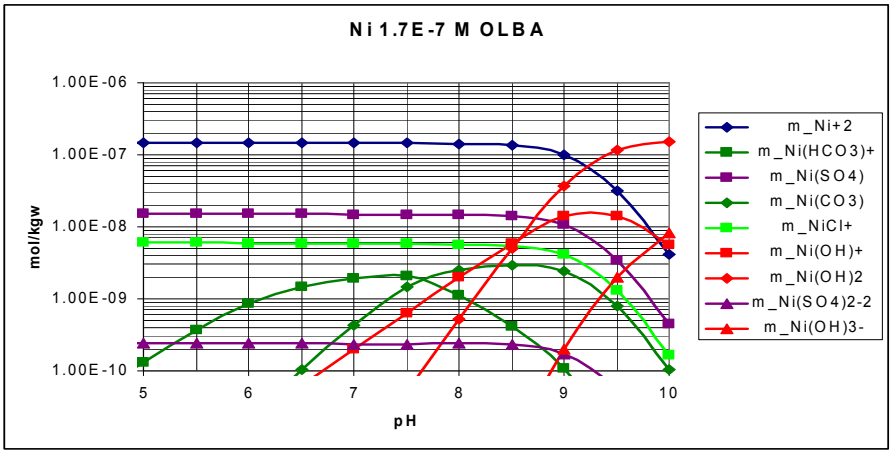

Figure Ni-3. *Soluble species of Ni in brackish OLBA (KR6-135) type water.*

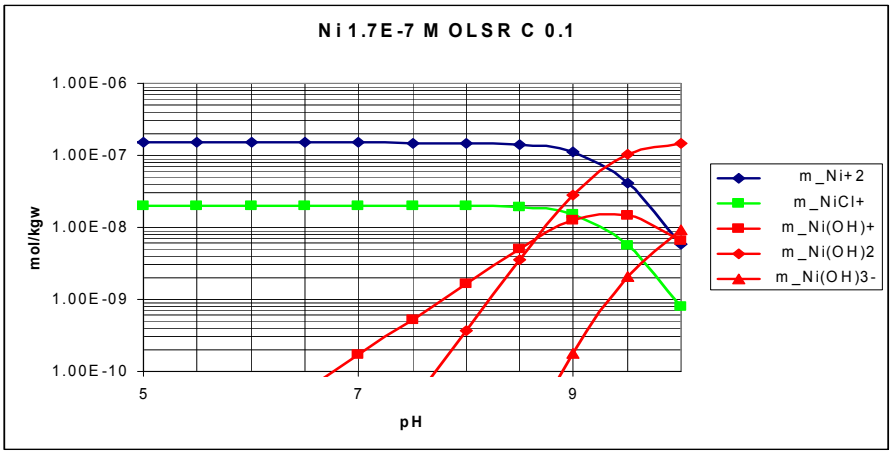

Figure Ni-4. *Soluble species of Ni in saline OLSR type water.*

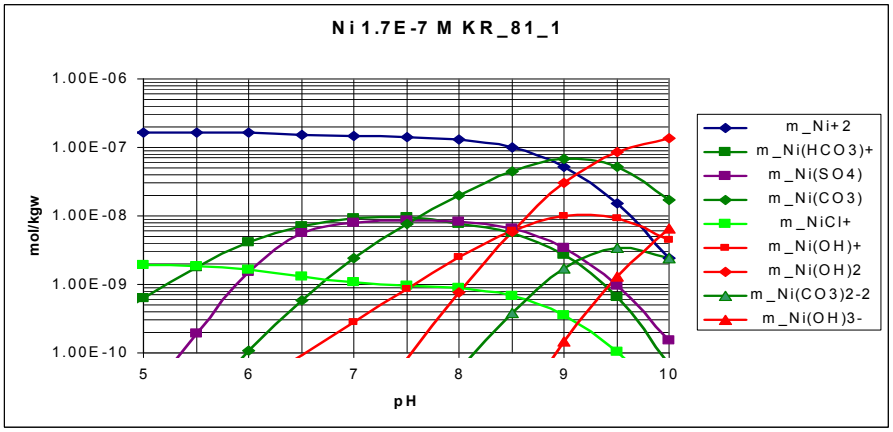

Figure Ni-5. *Soluble species of Ni in brackish KR4_81_1 water.*

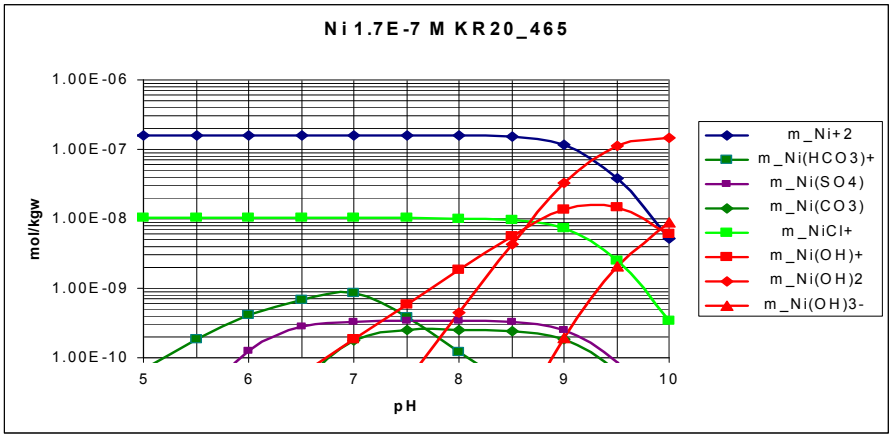

Figure Ni-6. *Soluble species of Ni in saline KR20_465_1 water.*

11.2 Sorption on rocks

11.2.1 Source data

The sorption mechanisms of Ni on silicate minerals are cation exchange and surface complexation. Sorption of Ni on the Olkiluoto granodiorite and mica gneiss has been determined in both 0.05 M and 0.5 M $NaClO_4$ (Olin et al. 2008). Sorption of Ni on biotites separated from the rocks was also determined. The R_d values for the crushed rocks and the R_d values derived from R_d values of the biotites are presented in Figures Ni-7 and Ni-8. They are used as the reference data for evaluation of sorption on the reference rocks.

Owing to sorption of Ni^{2+} at low pH being mainly by cation exchange, sorption at low pH is lower in higher ionic strength solutions. Typical of surface complexation, in the pH region of the sorption edge, the R_d values increase by one order of magnitude with an increase of pH by one unit. The sorption edge coincides with the formation of Ni-hydroxo complexes. It follows that K_d values are very dependent on the pH of the groundwaters.

The R_d values for Olkiluoto granodiorite and mica gneiss in the 0.05 M and 0.5 M $NaClO_4$ solutions are shown in Figures Ni-7a and Ni-7b. The R_d values for the mica gneiss are not clearly higher than for the granodiorite, as is suggested by the BET/N_2 surface areas (0.9 and 0.24 m^2/g). This is taken into account as an additional uncertainty. The R_d values for the rock types were nearly the same, indicating that the surface areas relevant for sorption cannot be very different. The K_d values for the reference rocks in $NaClO_4$ solutions were derived by using data for both granodiorite and mica gneiss (Figures Ni-7a – Ni-8b). In Figures Ni-8a and Ni-8b the R_d values are scattered. The smaller R_d value for a pH was selected for the derivation of sorption on the reference rocks.

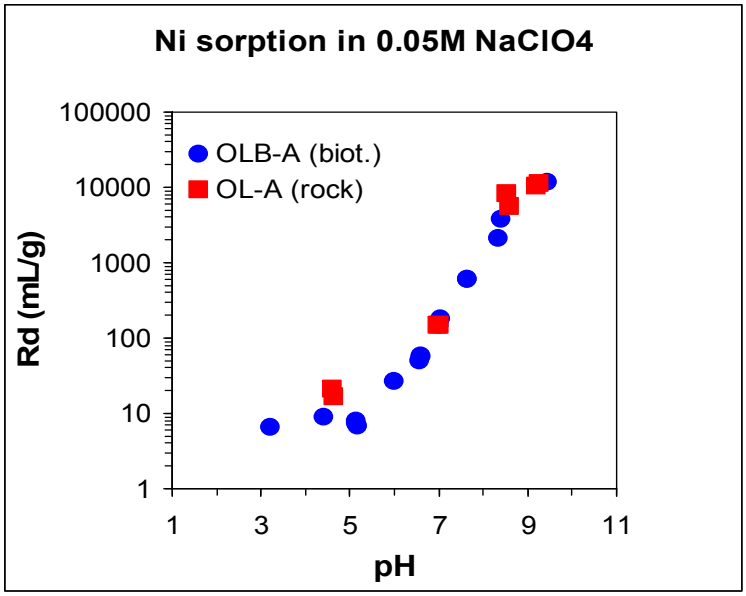

Figure Ni-7a. *R_d value (ml/g) of Ni for Olkiluoto granodiorite (OL-A) and calculated R_d value for the rock based on sorption on the separated biotite in 0.05 M $NaClO_4$ (Olin et al. 2008).*

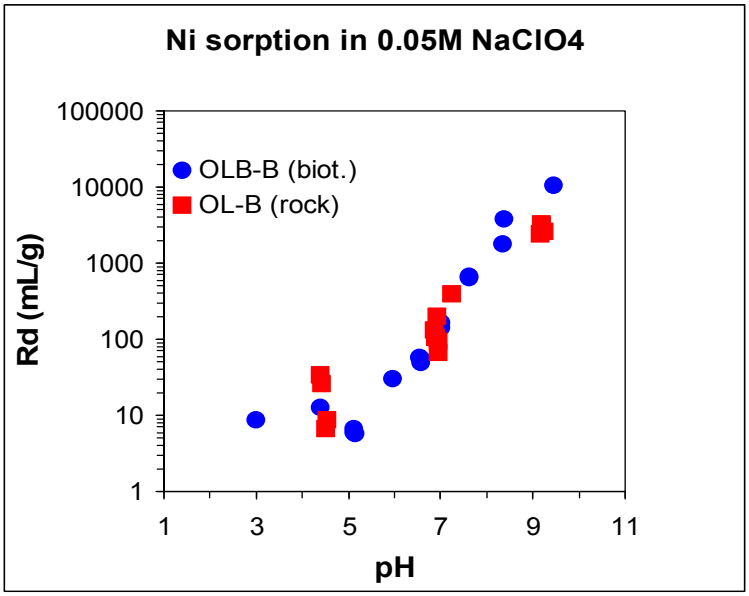

Figure Ni-7b. *R_d value (ml/g) of Ni for Olkiluoto mica gneiss (OL-B) and calculated R_d value for the rock based on sorption on the separated biotite in 0.05 M $NaClO_4$ (Olin et al. 2008).*

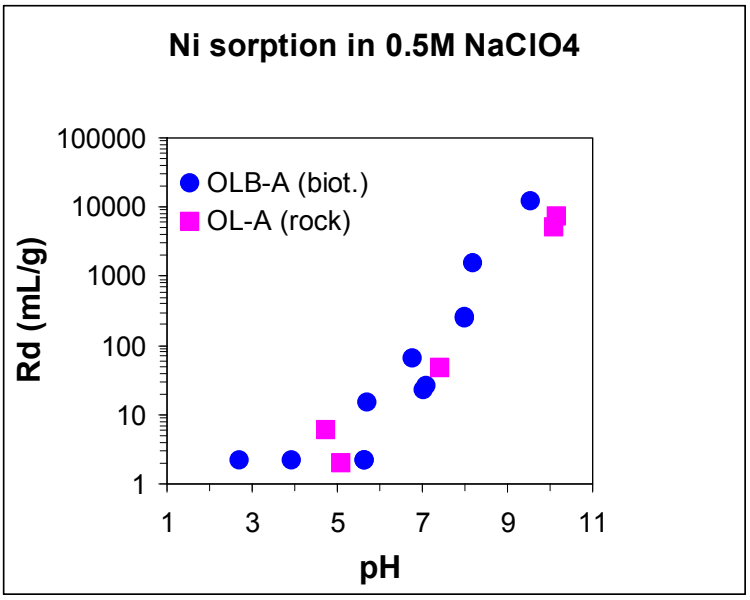

Figure Ni-8a. *R_d value of Ni for Olkiluoto mica gneiss (OLB) and calculated R_d value for the rock based on sorption on the separated biotite in 0.5 M $NaClO_4$ (Olin et al. 2008).*

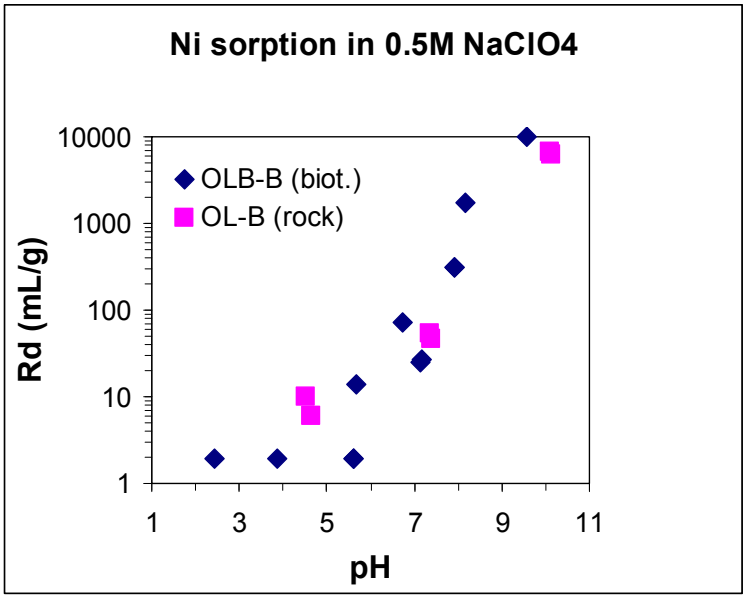

Figure Ni-8b. *R_d value of Ni for Olkiluoto mica gneiss (OLB) and calculated R_d value for the rock based on sorption on the separated biotite in 0.5 M $NaClO_4$ (Olin et al. 2008).*

K_d values of Ni in $NaClO_4$ solutions and in the groundwaters

The R_d values for the reference rocks in the $NaClO_4$ solutions were converted from the R_d values of the OLA and OLB rocks using the mica contents as the conversion factor. The R_d values for the reference rocks were converted to K_d values in perchlorate solution using the conversion factors given for the rocks (Chapter 3, Table 3-2). The calculated K_d for the $NaClO_4$ solution values are given in Figures Ni-9 and Ni-10.

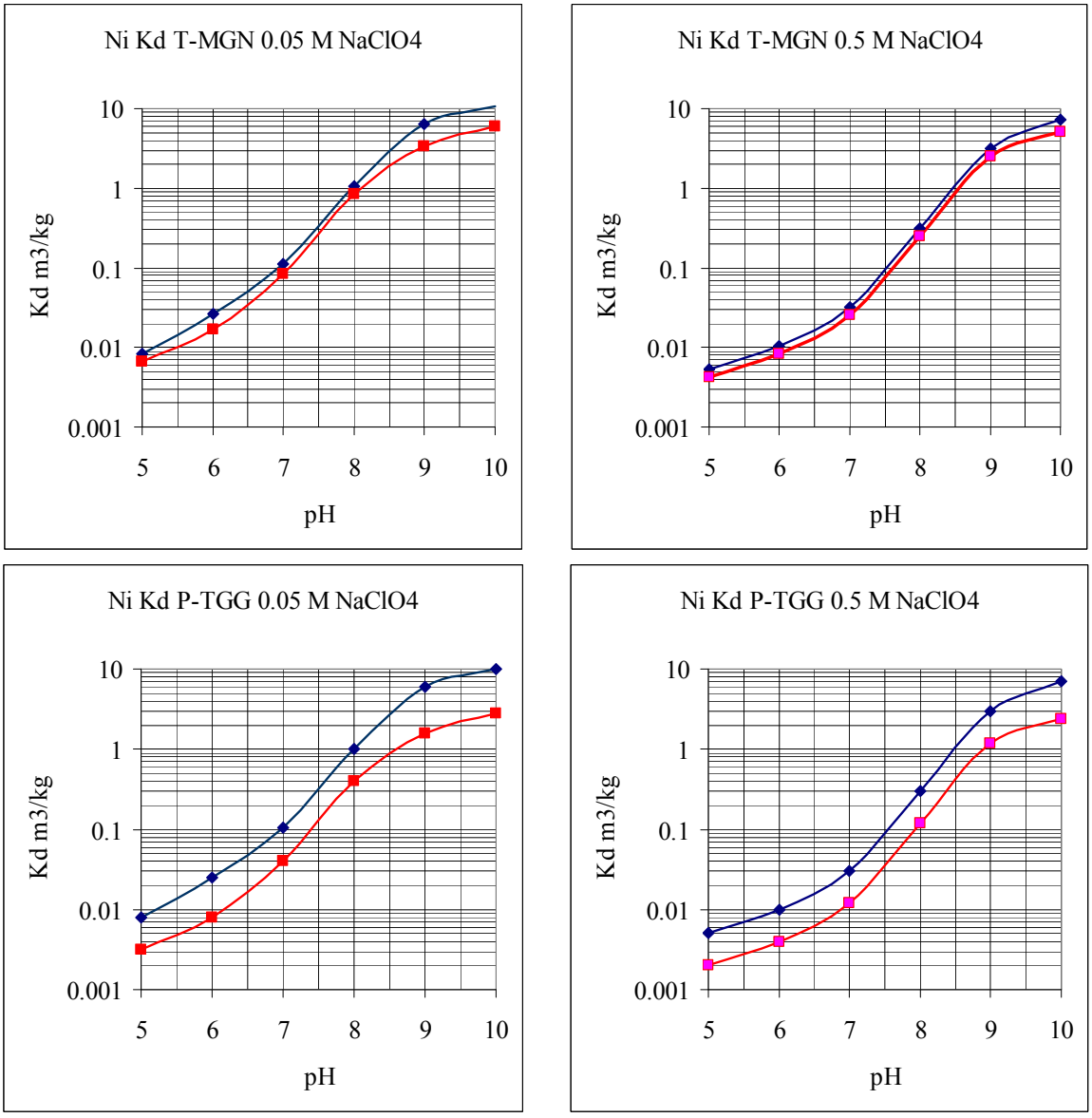

Figure Ni-9. *The calculated K_d values (m^3/kg) of Ni for rocks T-MGN (upper) and P-TGG (lower) in 0.05 M and 0.5 M $NaClO_4$ solutions. Diamonds= GD (granodiorite) Squares= MGN (mica gneiss)*

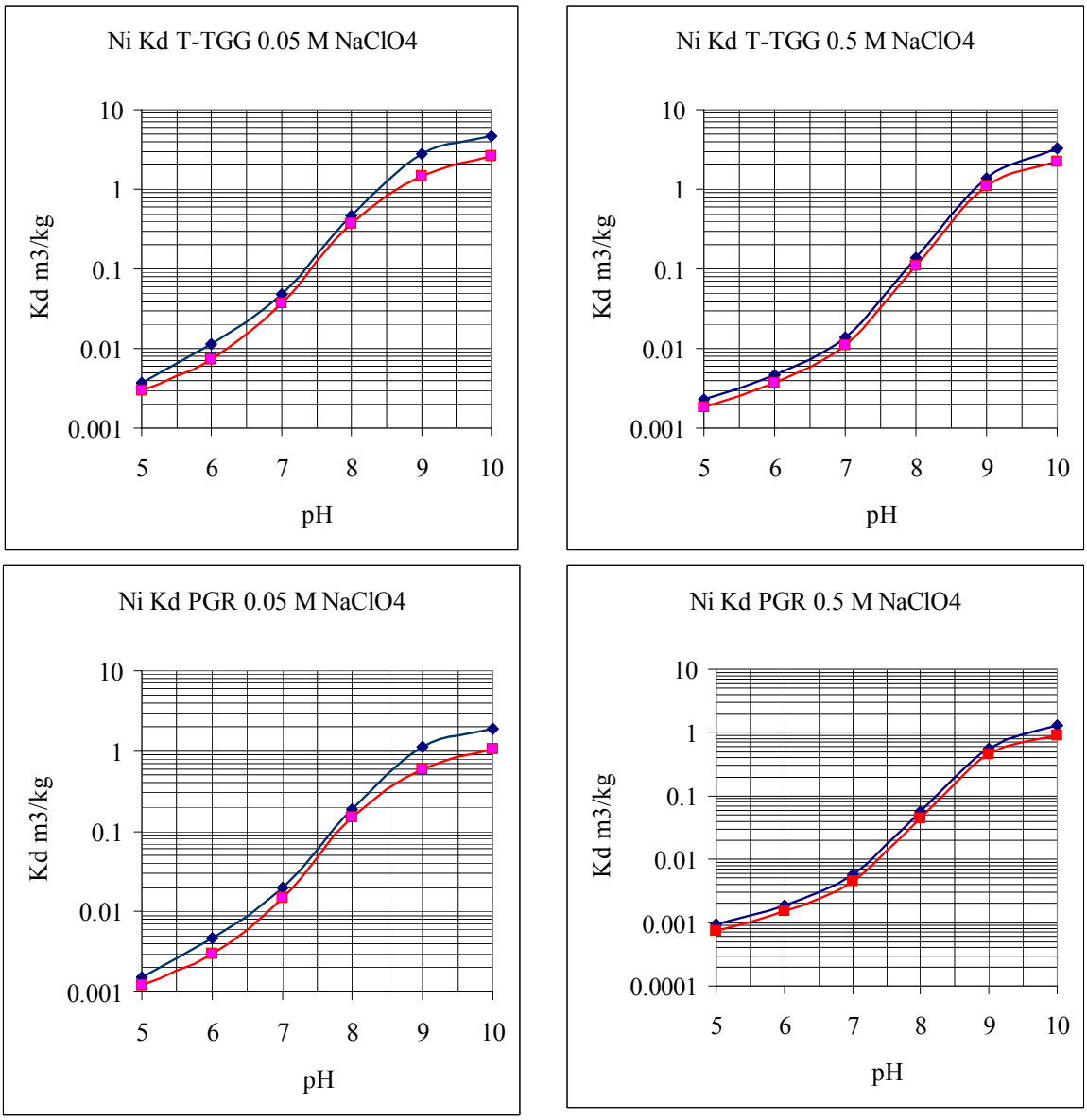

Figure Ni-10. *The calculated K_d values (m^3/kg) of Ni for rocks T-TTG (upper) and PGR (lower) in 0.05 M and 0.5 M $NaClO_4$ solutions. Diamonds= GD (granodiorite) Squares= MGN (mica gneiss)*

11.2.2 Best estimate K_d values

The main species of Ni in the pH range of the groundwaters is the Ni^{2+} ion. At pH 10 the proportion of sorbing hydroxo complexes is 90%. For the low-salinity waters OLGA and ALLMR, the values in 0.05 M $NaClO_4$ are suggested. No conversion for speciation is made, owing to the fact that the conversion is small and ionic strength in the source data is higher than in the low-salinity groundwaters, and competition in cation exchange is omitted.

Speciation of Ni in 0.5 M $NaClO_4$ solution differs from speciation in OLBA and KR4_81_1 waters, owing to the fact that the perchlorate ion does not form complexes with Ni^{2+}. The proportion of Ni^{2+} at pH 8 in these waters is 20 % lower than in $NaClO_4$ and at pH 10 the proportion of sorbing hydroxo complexes is 90 %. The values in 0.5 M $NaClO_4$ are suggested for these waters. No conversion for speciation is made owing to the fact that the conversion is small and ionic strength in the source data is higher than in the OLBA, and competition in cation exchange is omitted.

In the saline groundwater KR20_465_1, the proportion of Ni^{2+} and the hydroxo complexes are marginally different from those in the brackish waters and therefore no correction for speciation is made. The values in 0.5 M $NaClO_4$ are suggested for these waters.

The ionic strength of the saline water OLSR is higher than in the $NaClO_4$ solutions. The proportions of Ni^{2+} and the hydroxo complex at pH 8.3 and pH 10 are not very different from those in the brackish waters. No correction for speciation is made and the K_d values in 0.5 M $NaClO_4$ are suggested for this water.

Competition in sorption by Fe(II)

Ni concentration will most probably be very low in all groundwaters in far-field conditions. Groundwaters may contain di-valent transition element Fe(II) in a much higher concentration than Ni. The possible competition by Fe(II) in sorption to rocks is here evaluated.

In reducing groundwater, the Fe concentration in brackish Olkiluoto ground waters has been found to be 0.32–0.45 mg/L ($6–8 \cdot 10^{-6}$ M) and in the saline waters 0.02–0.13 mg/L. Including competition in sorption between Ni(II) and the natural Fe(II) ($2.4 \cdot 10^{-5}$ M) in groundwater in Opalinus clay gave a better fit to calculated the sorption isotherm as compared to the measured sorption. Competition between Fe and Ni reduced the K_d of Ni for Opalinus clay at pH 6 by a factor of around 2 (Bradbury & Baeyens 2011). The Fe concentrations in the Olkiluoto groundwater are lower than in the Opalinus water by a factor of at minimum 0.3, and the correction for K_d values at pH 6 is estimated to be much less than a factor of 2, based on the ratio of Fe(II) concentrations by a factor of 1.4 (Hellä et al. 2014). In addition, biotite is a iron rich mineral, and in the sorption experiments of Ni to biotite and crushed rock, the R_d values most probably include competition by Fe(II). It follows that no correction for Fe(II) in groundwater is made for the K_d values.

The best estimate K_d (m^3/kg) values of Ni for rocks are presented in Tables Ni-1–Ni-4.

Table Ni-1. *The best estimate K_d (m^3/kg) values of nickel for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-02**	**1.5E-02**	**2.9E+00**	**1.1E-01**	**6.0E-01**	**1.5E-01**	**7.0E-02**
10	5.9E+00	5.9E+00	5.9E+00	5.9E+00	5.9E+00	5.9E+00	5.9E+00

Table Ni-2. *The best estimate K_d values (m^3/kg) of nickel for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-03**	**7.5E-03**	**1.5E+00**	**5.5E-02**	**3.0E-01**	**7.5E-02**	**3.5E-02**
10	3.0E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00

Table Ni-3. *The best estimate K_d values (m^3/kg) of nickel for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.5E-03**	**6.5E-03**	**1.3E+00**	**7.0E-02**	**2.6E-01**	**8.0E-02**	**2.9E-02**
10	2.6E+00	2.6E+00	2.6E+00	2.6E+00	2.6E+00	2.6E+00	2.6E+00

Table Ni-4. *The best estimate K_d values (m^3/kg) of nickel for pegmatic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.6E-03**	**2.6E-03**	**5.1E-01**	**2.0E-02**	**3.5E-01**	**3.0E-02**	**1.2E-02**
10	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00

11.2.3 Lower limit K_d values

The lower limit K_d values were calculated by dividing the best estimate value by an uncertainty factor. The lower limit values for T-MGN, P-TGG, T-TGG and PGR rocks are presented in Tables Ni-6 – Ni-9.

The uncertainty arises from mineralogical differences in the rocks, and from the fact that the sorption edge of Ni coincides with the pH range of the reference waters. For K_d in OLBA and KR4_81_1 waters, the complexity of the calculated speciation is an additional source of uncertainty when there are no R_d values. The best estimate values

are conservatively proposed based on source data in higher ionic strength (I.S.) than the reference waters and no uncertainty for differences in I.S. is taken into account. The uncertainties owing to differences in speciation are small and are not taken into account. The uncertainties mainly originate from the pH dependence of the R_d values and mineralogical uncertainties. The source data was from sorption to biotites and to crushed Olkiluoto mica gneiss and granodiorite. The uncertainty factor for conversion of sorption to rocks from data to biotite is 8. Combined with the uncertainty factor (2.26) from the pH dependency of K_d at pH 7-9 (log slope K_d/pH =1), this yields a total uncertainty factor of 18. At pH 5.8 the I.S. dependency of sorption is highest. Including this with the pH originating uncertainty, the uncertainty factor is estimated to be 2.5 and the total uncertainty factor becomes 20. This value is used for T-MGN, P-TGG and T-TGG. For PGR, the mineralogical uncertainty is so large that a total uncertainty factor of 50 is proposed for this rock. The uncertainty factors for the reference rocks are presented in Table Ni-5.

Table Ni-5. *The uncertainty factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	20
T-TGG	20
P-TGG	20
PGR	50

Table Ni-6. *The lower limit K_d values (m^3/kg) of nickel for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-04**	**7.5E-04**	**1.5E-01**	**5.5E-03**	**3.0E-02**	**7.5E-03**	**3.5E-03**
10	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01

Table Ni-7. *The lower limit K_d values (m^3/kg) of nickel for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.8E-04**	**3.8E-04**	**7.5E-02**	**2.8E-03**	**1.5E-02**	**3.8E-03**	**1.8E-03**
10	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01

Table Ni-8. *The lower limit K_d values (m^3/kg) of nickel for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.3E-04**	**3.3E-04**	**6.5E-02**	**3.5E-03**	**1.3E-02**	**4.0E-03**	**1.5E-03**
10	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01

Table Ni-9. *The lower limit K_d values (m^3/kg) of nickel for pegmatic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.2E-05**	**5.2E-05**	**1.0E-02**	**4.0E-04**	**7.0E-03**	**6.0E-04**	**2.4E-04**
10	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02

11.3 Sorption on clays

11.3.1 Source data

Kaolinite

Sorption of Ni on kaolinite KGa-1b has been determined in 0.001 M, 0.01 M and 0.1 M $NaNO_3$ solutions at pH range 5–9 (Puukko and Hakanen 1998). The values in the different solutions (Figure 5 in Puukko and Hakanen 1998) indicate a strong dependence of R_d on the ionic strength and on the pH. The R_d values in the non-complexing $NaNO_3$ solution were corrected for speciation of Ni in the reference waters by a fraction of sorbing species (FSS), which is the sum of the fraction of Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$ of total Ni. The R_d values of 0.001 M $NaNO_3$ were used for glacial reference water OLGA and the R_d values of 0.1 M $NaNO_3$ for the other reference waters. The R_d values of $NaNO_3$ solutions were multiplied by the FSS to calculate the K_d values for the reference waters. $Ni(OH)_3^-$ is included in the FSS because its impact is included in the sorption edge source data. The proportion of $Ni(OH)_3^-$ on speciation in the groundwaters is negligible at the pH of the waters and is minor also at pH 10 (Table Ni-10).

Table Ni-10. *The calculated K_d values (m^3/kg) of nickel for kaolinite KGa-1b in reference waters. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
pH	5.8	8.8	7.6	8.3	7.8	7.4
FSS	1.00	0.74	0.93	0.90	0.81	0.94
R_d (m^3/kg)	1	10	0.7	6	1.2	0.35
Kd (m^3/kg)	1	7.4	0.65	5.4	0.97	0.33
	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
pH 10	10	10	10	10	10	10
FSS	1.00	0.96	0.99	0.99	0.88	0.99
R_d (m^3/kg)	15	15	15	15	15	15
K_d (m^3/kg)	15	14	15	15	13	15
FSS = Sum of Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$, $Ni(OH)_3^-$ of total Ni						

Illite

The source data for illite IMt-1 was from a study (Poinssot et al. 1999, Bradbury and Baeyens 2009) on sorption of Cs, Sr, Ni and Eu on Na-illite. The values of Ni in 0.01 M $NaClO_4$ solution were used for glacial OLGA and fresh ALLMR waters. For other reference waters the values of Ni in 0.1 M $NaClO_4$ were used. The selected R_d values are presented in Table Ni-11. The FSS factor was used to convert the K_d values of Ni for illite IMt-1 in the reference waters, as in the case of kaolinite KGa-1b (Table Ni-10).

Table Ni-11. *The selected source data R_d (m^3/kg) values of Ni for illite (Poinssot et al. 1999).*

Reference water	pH	m^3/kg
OLGA, ALLMR : 0.01 M $NaClO_4$	6	7
	8.8	16
Other waters: 0.1 M $NaClO_4$	7–10	10

Table Ni-12. *The calculated K_d values (m^3/kg) of nickel for illite IMt-1 in reference waters. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
pH	5.8	8.8	8.3	7.6	7.8	7.4
FSS	1.00	0.74	0.93	0.90	0.81	0.94
Rd (m^3/kg)	7	16	10	10	10	10
Kd (m^3/kg)	7	12	9.3	9	8.1	9.4
	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
pH	10	10	10	10	10	10
FSS	1.00	0.96	0.99	0.99	0.88	0.99
Rd (m^3/kg)	16	16	10	10	10	10
Kd (m^3/kg)	16	15	9.9	9.9	8.8	9.9
FSS = Sum of Ni^{2+}, $Ni(OH)^+$, $Ni(OH)_2$ of total Ni						

11.3.2 Best estimate K_d values

The best estimate K_d values of nickel for kaolinite and illite in the Olkiluoto geosphere are presented in Tables Ni-13 and Ni-14.

Table Ni-13. *The best estimate K_d (m^3/kg) values of nickel for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+00**	**1.0E+00**	**5.9E+00**	**6.5E-01**	**5.4E+00**	**1.0E+00**	**3.3E-01**
10	1.5E+01	1.5E+01	1.4E+01	1.4E+01	1.4E+01	1.3E+01	1.4E+01

Table Ni-14. *The best estimate K_d (m^3/kg) values of nickel for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E+00**	**7.0E+00**	**1.2E+01**	**9.0E+00**	**9.3E+00**	**8.1E+00**	**9.4E+00**
10	1.6E+01	1.6E+01	1.5E+01	9.9E+00	9.9E+00	8.8E+00	9.9E+00

11.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(Ni-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Ni-2)}$$

The uncertainty factors are collected in Tables Ni-15 and Ni-17.

Kaolinite

UF_{tot}= 11 the total uncertainty factor for glacial OLGA/OLGO waters.

UF_{tot}= 10 for other reference waters.

UF_{source}= 1.6. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for kaolinite were calculated. The factor 1.6 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1. Cation exchange capacity was not relevant here and so the factor is 1.

UF_{spec}= 1.4 as proposed in Hummel and Berner (2002).

UF_{pH}= 2.5. The uncertainty factor of pH on the R_d values for OLGA and OLGO waters (Figure 5 in Puukko and Hakanen 1998). The value is based on scatter of data.

UF_{pH}= 2.26 for other reference waters.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of nickel for kaolinite in the Olkiluoto geosphere are presented in Table Ni-16.

Table Ni-15. *The factors used for calculation of the lower limit values of nickel for kaolinite . KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite					
Water	UF_{source}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}
OLGA	1.6	1.4	2.5	2	11
OLGO	1.6	1.4	2.5	2	11
ALLMR	1.6	1.4	2.26	2	10
OLBA	1.6	1.4	2.26	2	10
OLSR	1.6	1.4	2.26	2	10
KR4	1.6	1.4	2.26	2	10
KR20	1.6	1.4	2.26	2	10

Table Ni-16. *The lower limit K_d (m^3/kg) values of nickel for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**9.1E-02**	**9.1E-02**	**5.9E-01**	**6.5E-02**	**5.4E-01**	**1.0E-01**	**3.3E-02**
10	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.3E+00	1.4E+00

Illite

UF_{tot}= 11 the total uncertainty factor for ALLMR and OLSR waters.

UF_{tot}= 15 for other reference waters.

UF_{source}= 2. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the R_d values, from which the best estimate K_d values for illite were calculated. The factor 2 is used for the source data from the literature (Poinssot et al. 1999).

UF_{model}= 1. No model was used.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity (UF_{CEC}) covers the differences between the IMt-1 illite and natural illites (Bradbury and Baeyens 2003, Missana et al. 2008).

UF_{spec}= 1.4 The uncertainty of speciation as proposed in Hummel and Berner (2002).

UF_{pH}= 1.5 the uncertainty factor of pH for the R_d values for ALLMR and OLSR waters.

UF_{pH}= 2.1 for other reference waters.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of nickel for illite in Olkiluoto geosphere are presented in Table Ni-18.

Table Ni-17. *The factors used for calculation of the lower limit values for illite in Olkiluoto geosphere. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite						
Water	UF_{source}	UF_{CEC}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}
OLGA	2	1.3	1.4	2.1	2	15
OLGO	2	1.3	1.4	2.1	2	15
ALLMR	2	1.3	1.4	1.5	2	11
OLBA	2	1.3	1.4	2.1	2	15
OLSR	2	1.3	1.4	1.5	2	11
KR4	2	1.3	1.4	2.1	2	15
KR20	2	1.3	1.4	2.1	2	15

Table Ni-18. *The lower limit K_d (m^3/kg) values of nickel for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.7E-01**	**4.7E-01**	**1.1E+00**	**6.0E-01**	**8.5E-01**	**5.4E-01**	**6.3E-01**
10	1.1E+00	1.1E+00	1.4E+00	6.6E-01	9.0E-01	5.9E-01	6.6E-01

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12 SELENIUM

12.1 Speciation

Selenium in nature

Selenium is a group VIb element and exists in nature in oxidation states –II, 0, IV and VI. In oxidation states –II and VI, there are many similarities with the lighter VIb element, sulphur. Selenium is found in rocks often associated to sparingly soluble sulphide minerals such as CuS and PbS.

In the Finnish groundwaters, selenate Se(VI) and selenite Se(IV) were the main species (70% and 30%) in the waters with the highest Se concentrations (Alfthan et al. 1995). In drilled wells, the median Se concentration was 160 ng/L ($1.5 \cdot 10^{-9}$ M) and in dug wells around 50 ng/L ($5 \cdot 10^{-10}$ M). The highest values were found near Hämeenlinna, where the rock type is black schist (Lahermo et al. 2002). The Se concentration in saline groundwaters at Olkiluoto was $3 \cdot 10^{-7}$ M to $1.6 \cdot 10^{-6}$ M (Hellä et al. 2014). The maximum concentration found was $1.3 \cdot 10^{-5}$ M. There are no data on the oxidation states of Se in the Olkiluoto groundwaters. The calculated solubility was $<10^{-9}$ M to $FeSe_2$ (ferroselite), as the solubility limiting phase in the Olkiluoto groundwaters in Grivé et al. (2008). Solubility of amorphous and crystalline Se(0) in reducing environmental conditions is $1 \cdot 10^{-9}$ M to $1 \cdot 10^{-8}$ M (Maes et al. 2004). The Se concentration in the Olkiluoto groundwaters is higher than these values and the solubility of Se is thus not limited by amorphous or crystalline Se(0) or ferroselite.

The abiotic homogenous reduction of selenite or selenate to selenide may be very slow and the reduction in the geosphere is most probably microbe-mediated, as with the reduction of sulphate to sulphide (Myneni et al. 1997, Herbel et al. 2003, Hockin & Gadd 2003). Microbial reduction of the selenium oxyanions to Se(0) is an important process for controlling the behaviour of selenium in the biosphere (Dridge et al. 2007). Metallic iron and green rust are able to induce a heterogeneous reduction of Se(VI) to Se(0) followed by the formation of magnetite (Myneni et al. 1997). Magnetite itself is not capable of the reduction of Se(VI) to lower oxidation states (Puranen et al. 2009, 2010). Se(IV) is more readily reduced to Se(0) or Se(-II) when metallic iron surfaces are exposed to solution. Reactions of this kind are not expected in far-field conditions. In the shallow groundwaters at Olkiluoto, sulphate is the main species of sulphur (as an analogue to selenium), and thus a conservative estimate is that the reduction of selenate or selenite to Se(0) and selenide is negligible in shallow waters.

Speciation in reference waters

The speciation of Se was calculated in reducing saline OLSR reference water, anoxic glacial meltwater OLGA, oxic glacial meltwater OLGO and fresh ALLMO reference water for an Se concentration of $1 \cdot 10^{-7}$ M using ANDRA's Thermo_Chimie Version 7b database (Figures Se-1 – Se-7) (ANDRA 2009).

The soluble Se species are anionic in the form of selenide HSe^- in reducing conditions and polyselenides Se_4^{2-} and Se_3^{3-} in mildly reducing waters. In less reducing to

oxidising conditions, selenous acid (H_2SeO_3) and selenic acid (H_2SeO_4) and their dissociated oxoanion species, selenite SeO_3^{2-} and selenate SeO_4^{2-}, are the most abundant.

In the fresh mildly reducing ALLMR reference water in equilibrium with $CaSeO_3 \cdot H_2O$ (pK_s -7.76) (Seby et al. 2001), the calculated Se concentration is about $7 \cdot 10^{-3}$ M and the main species are selenate (70 %) and selenite (30 %), in good agreement with the measured speciation in Finnish groundwaters (Alfthan et al. 1995). Alkaline earth selenates are minor species in oxic fresh reference water ALLMO (Figure Se-7).

Speciation of Se in the water is not dependent on water salinity or carbonate concentration. The speciation is the same in all reducing waters and in all oxic waters.

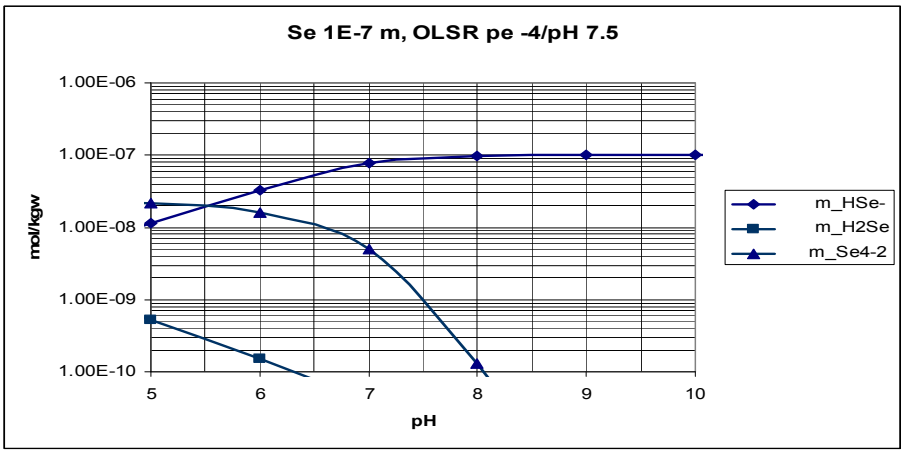

Figure Se-1. *Selenium speciation under reducing conditions in saline OLSR reference water.*

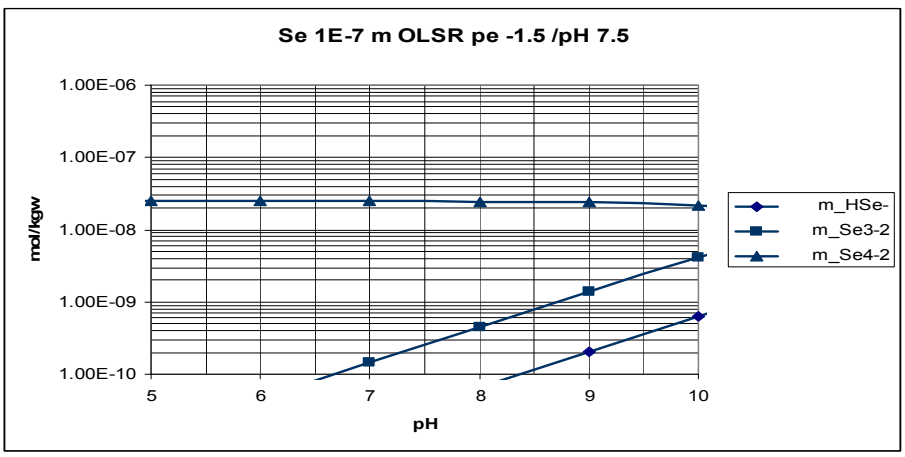

Figure Se-2. *Selenium speciation under mildly reducing conditions in saline OLSR reference water. The main species is polyselenide.*

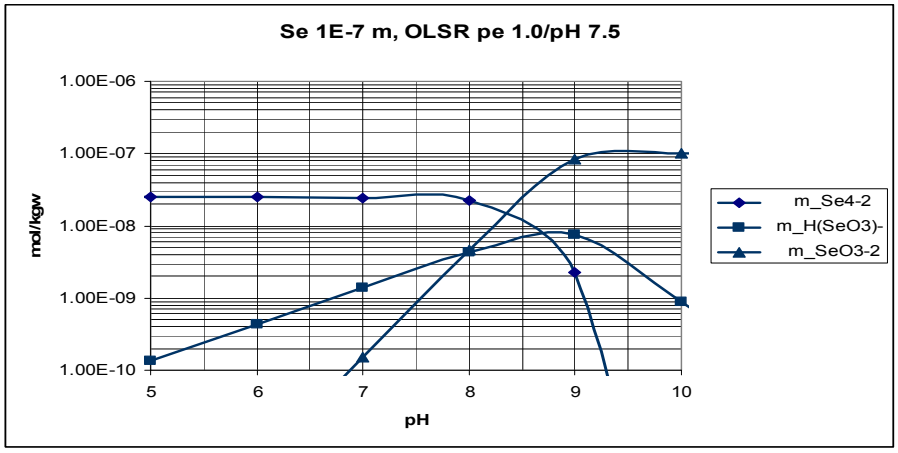

Figure Se-3. *Selenium speciation under mildly reducing conditions in saline OLSR reference water. The main species is polyselenide up to pH 8.3 and forms of selenite at higher pH.*

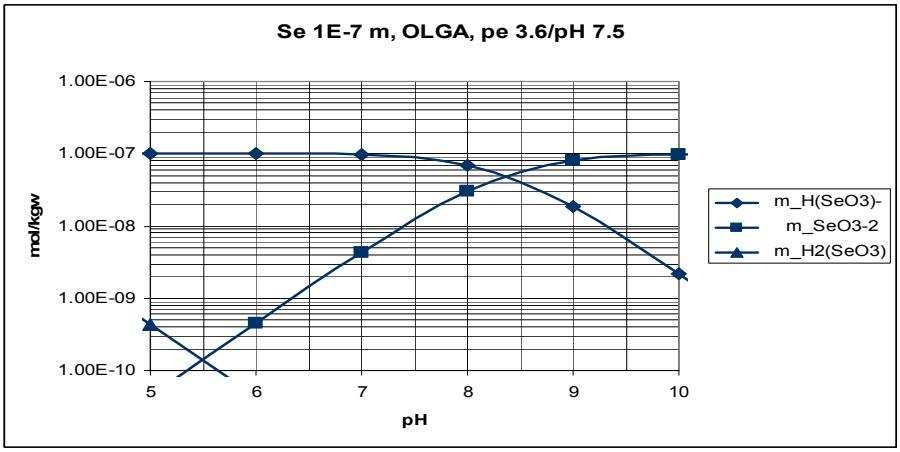

Figure Se-4. *Selenium speciation under anoxic conditions in glacial meltwater OLGA.*

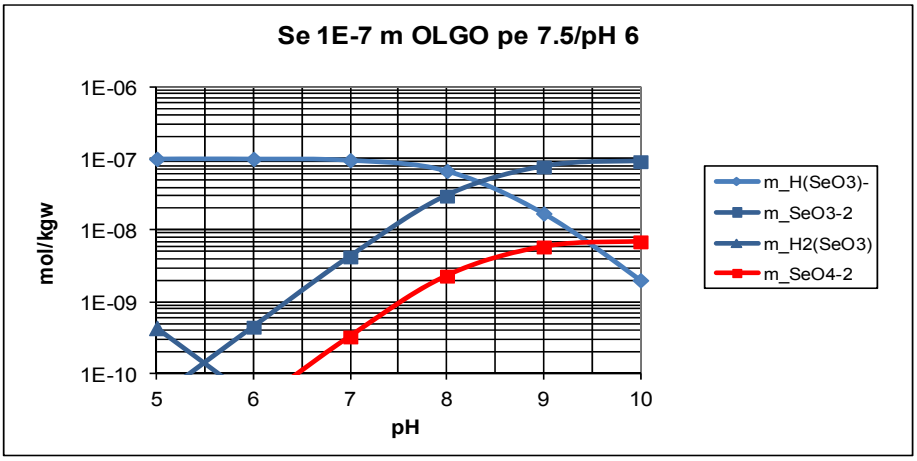

Figure Se-5. *Selenium speciation under anoxic/oxidising conditions in glacial meltwater OLGO.*

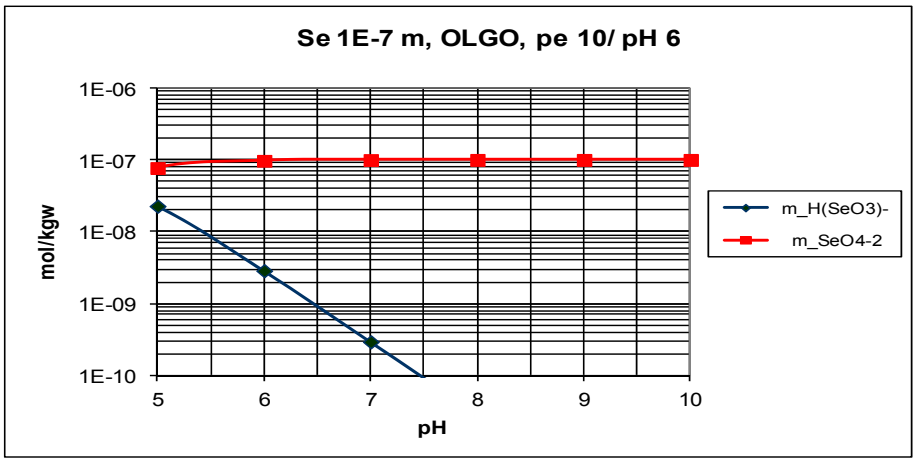

Figure Se-6. *Selenium speciation under oxidising conditions in glacial meltwater OLGO.*

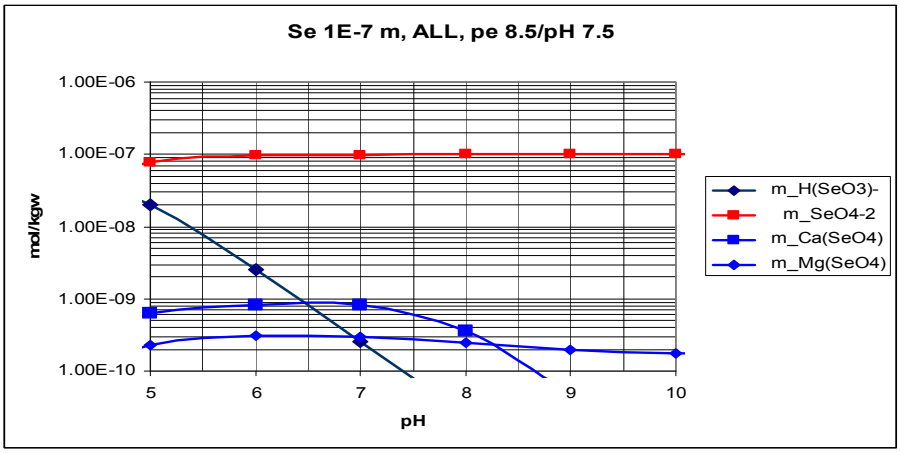

Figure Se-7. *Selenium speciation in fresh ALLMO reference water under oxidising conditions.*

12.2 Sorption on rocks

There are no data on the sorption of selenide (HSe^-) by aluminosilicates or rocks. Under reducing conditions, the thermodynamically stable Se species are Se(0) and HSe^- and anionic Se-polymers such as Se_4^{2-}. HSe^- is the main sorbing species. Relatively high HS^- analogue concentrations are found in some Olkiluoto groundwaters, which suggests that the sorption of HSe^- is low. Under reducing conditions, selenide was efficiently sorbed on pyrite as Se(0) (Liu et al. 2008). The R_d values decreased from 60 m^3/kg to 7 m^3/kg in equilibrium with Se concentration $1 \cdot 10^{-7}$ M and $5 \cdot 10^{-6}$ M. In some OL groundwaters, total sulphide (S^{2-} chemical analogue to Se^{2-}) concentration is $1 \cdot 10^{-3}$ M. Removal of selenide, chemically very similar to sulphide, from groundwater by sorption on pyrite is thus not expected to be very efficient at Olkiluoto. There are no data on sorption of polyselenides or polysulphides on silicate minerals, and selenium in this form in this report is taken to behave in the same way as selenide. The removal mechanism of Se(0) from water is most probably more due to low-solubility Se-solids or incorporation to solids like FeSSe and $FeSe_2$ than to sorption.

The oxoanions, selenite and selenate, undergo sorption by ligand exchange with iron oxide minerals and ferric hydroxide (Dzombak & Morel 1990). The sorption is pH-dependent and selenate is sorbed only at a pH lower than pH 7. Since the pH of groundwaters is typically higher than this value, sorption of selenate is very low. Selenite, in turn, is sorbed on ferric hydroxide at a pH lower than pH 9, but on iron containing silicate minerals (biotite, chlorite) the sorption can be detected only at a pH below pH 8 (Tachi et al. 1998). Sorption of selenite on volcanic tuff (Tachi et al. 1998) shows pH dependence typical of the sorption of anions on ferric oxide, the R_d values being 0.001- 0.022 m^3/kg at pH 8.0 - 8.5.

The sorption of trace concentration of selenite at pH 7.9 - 9.0 on Lac du Bonnet granite in saline groundwater has R_d values between 0 and 8.9 ml/g (0 - 0.0089 m^3/kg) (Ticknor & McMurry 1996). This low sorption is in agreement with the R_d values of around $5 \cdot 10^{-4}$ m^3/kg for K-feldspar, smectite and quartz at pH 7 - 9 in 0.1 M NaCl in Tachi et al. (1998).

12.2.1 Source data

Sorption of Se on crushed Olkiluoto T-series mica gneiss T-MGN, Olkiluoto P-series tonalite granodiorite granite gneiss P-TGG, Olkiluoto T-series tonalite granodiorite granite gneiss T-TGG and Olkiluoto pegmatitic granite PGR was determined under anoxic (N_2-glove-box) conditions at pH 6 to pH 10 in OLGA, ALLMR, OLBA and OLSR reference waters (Methodology described in Appendix 4). In addition, sorption was determined in oxic conditions at pH 7 to pH 10 in oxic OLGO, ALLMO and OLSO reference waters. Sorption on the rocks is given in Figures Se-8 – Se-15. The low initial pH tends to be buffered to higher values and the initial pH of 10 to a lower value.

Base on the literature (Myneni et al. 1997, Herbel et al. 2003, Hockin & Gadd 2003) on the reduction of the Se-oxyanions to Se(0) and Se(II) only by green rust or microbes, it was concluded that the species in the experiments were SeO_4^{2-} and SeO_3^{2-}. So as not to overestimate sorption, it was assumed that under oxic conditions the SeO_4^{2-} was the dominant solution species and under anoxic conditions the solution species was SeO_3^{2-}. As a conservative approach in reducing conditions, it was estimated that Se(-II) is the main species and its sorption was estimated as very low.

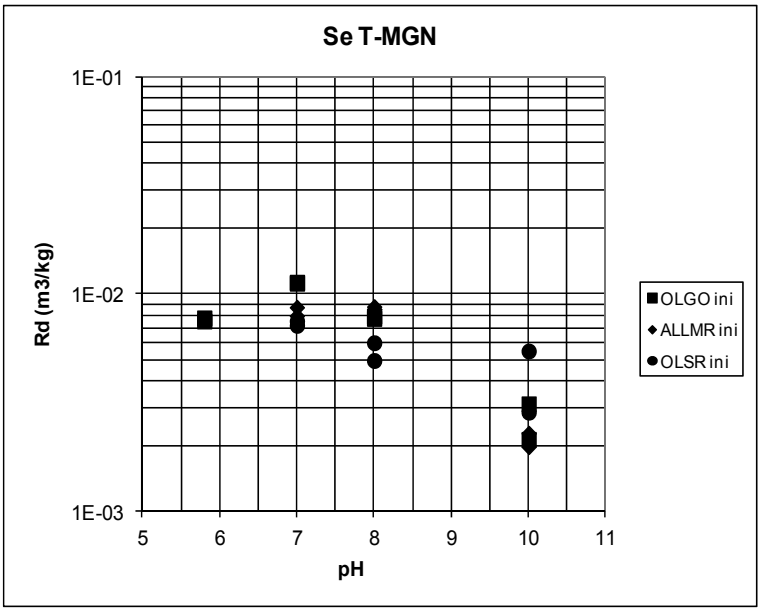

Figure Se-8. *R_d values (m^3/kg) of selenium for Olkiluoto T-series mica gneiss T-MGN in oxic conditions. pH is the initial pH(i) at the experiment.*

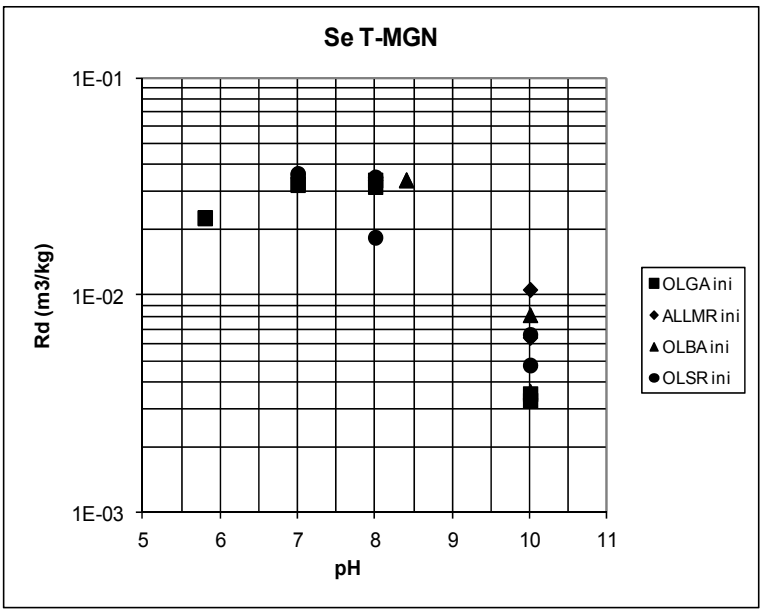

Figure Se-9. *R_d values (m^3/kg) of selenium for Olkiluoto T-series mica gneiss T-MGN in anoxic conditions. pH is the initial pH(i) at the experiment.*

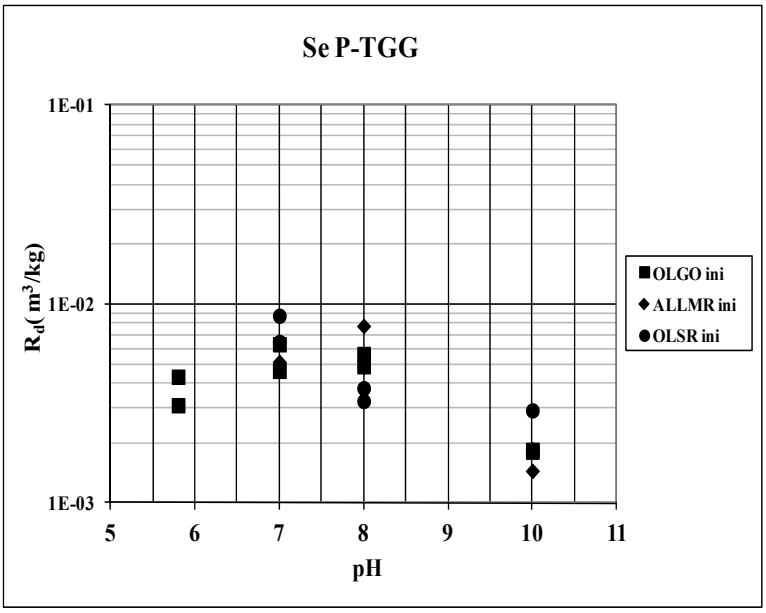

Figure Se-10. *R_d values (m^3/kg) of selenium for Olkiluoto P-series tonalite granodiorite granite gneiss P-TGG in oxic conditions. pH is the initial pH(i) at the experiment.*

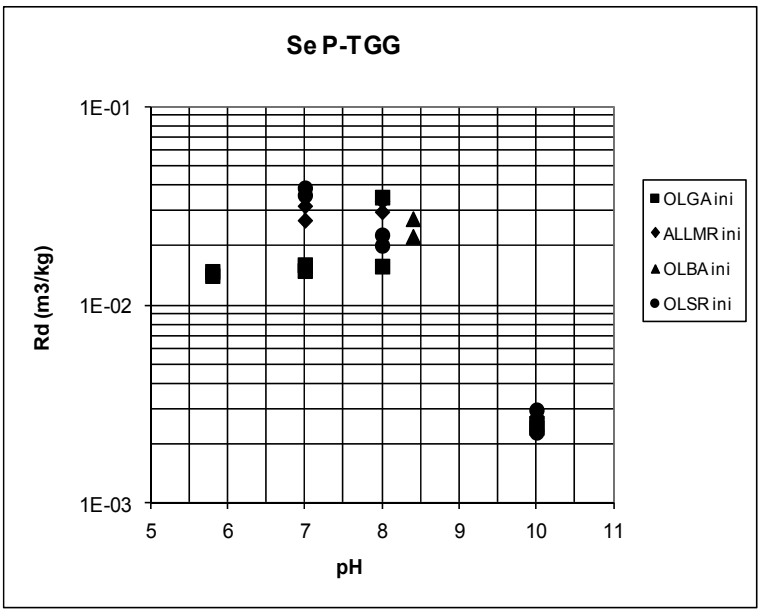

Figure Se-11. *R_d values (m^3/kg) of selenium for Olkiluoto P-series tonalite granodiorite granite gneiss P-TGG in anoxic conditions. pH is the initial pH(i) at the experiment.*

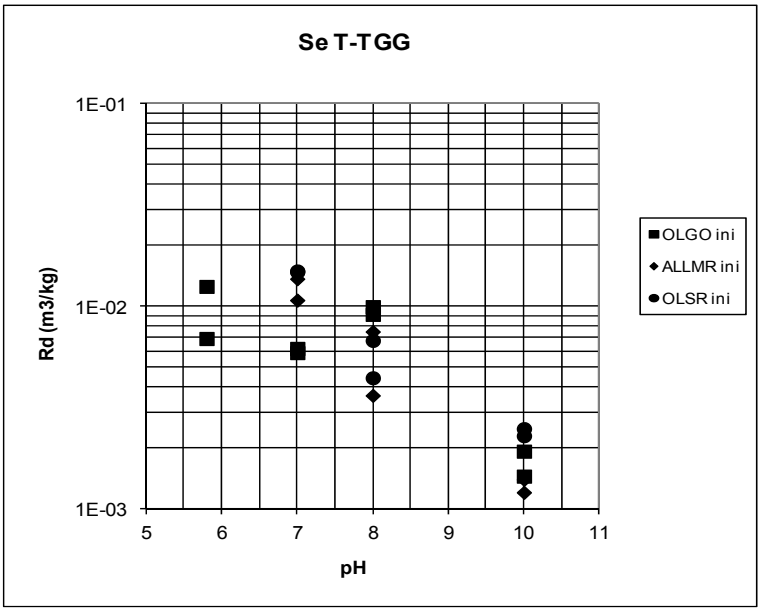

Figure Se-12. *R_d values (m^3/kg) of selenium for Olkiluoto T-series tonalite granodiorite granite gneiss T-TGG in oxic conditions. pH is the initial pH(i) at the experiment.*

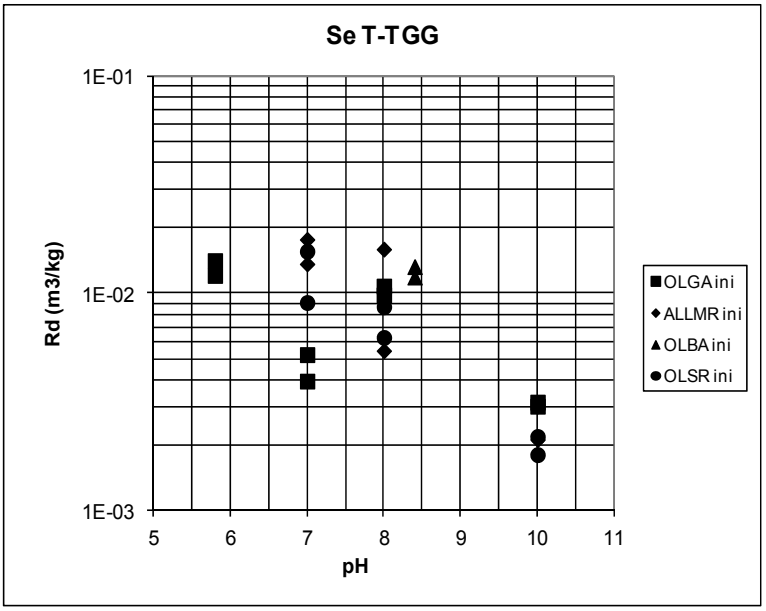

Figure Se-13. *R_d values (m^3/kg) of selenium for Olkiluoto T-series tonalite granodiorite granite gneiss T-TGG in anoxic conditions. pH is the initial pH(i) at the experiment.*

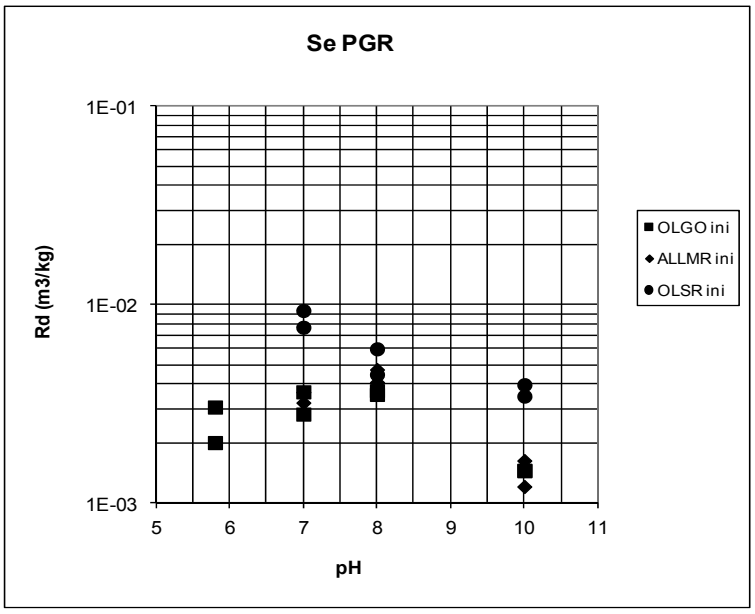

Figure Se-14. *R_d values (m^3/kg) of selenium for Olkiluoto pegmatitic granite PGR in oxic conditions. pH is the initial pH(i) at the experiment.*

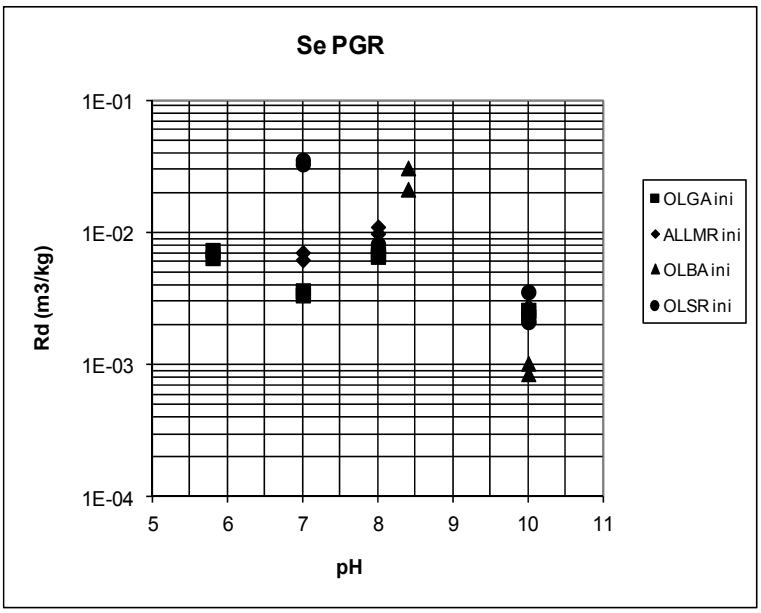

Figure Se-15. *R_d values (m^3/kg) of selenium for Olkiluoto pegmatitic granite PGR in anoxic conditions. pH is the initial pH(i) at the experiment.*

12.2.2 Best estimate K_d values

The best estimate K_d values were calculated from the R_d values using the R_d to K_d conversion factors for the reference rocks (see Chapter 3). The R_d values at initial experimental pH were used. This gives more conservative values for the groundwaters.

There is a clear pH dependency in the R_d values (Figs. Se-8 – Se-15). As pH increases, the negative surface charge increases, thus the adsorption of selenium oxyanions is decreased. There are no data on sorption of polyselenides or polysulphides on silicate minerals, and selenium in this form is taken to behave like selenide in this report. In the experimental oxic and anoxic solutions, only oxoanion Se-species selenate and selenite are expected. Under oxic and anoxic conditions, pH dependencies in sorption were taken into account by dividing pH region into two parts. At a pH lower than pH 8, the R_d values were nearly the same, and in this region the lowest R_d value was chosen as the best estimate for each rock type and water. Between pH 8 and pH 10, a linear decrease in R_d values was assumed. The best estimate R_d values were chosen between the lowest experimental values. For OLGA and OLGO glacial meltwaters at pH 5.8 the R_d value at pH 7 is chosen.

The speciation of Se in brackish KR4_81_1 and saline KR20_465_1 groundwaters is similar to ALLMR and OLSR reference waters respectively. A difference in carbonate concentration does not alter speciation. The same best estimate K_d values for groundwaters are taken as for the corresponding reference water (Tables Se-1 – Se-4).

Iida et al. (2011) studied the sorption of Se(-II) on granodiorite under reducing conditions. The batch experiments were performed on rock disks at pH 8.5 to 11.5 in groundwater. The reducing conditions were maintained by hydrazine. Sorption of selenium species HSe^- and Se_4^{2-} was observed and biotite was suggested to dominate the sorption of selenide. Although Iida et al. (2011) reported the sorption of reduced species of Se, we assume here that these species do not sorb and therefore remain on the conservative side in our selections for the best estimates.

In reducing conditions, sorption behaviour of selenium as selenide is taken to be very low. Therefore no best estimate K_d value for Se in reducing conditions is given.

Table Se-1. *Best estimate K_d values (m^3/kg) of selenium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**7.4E-03**	**1.8E-03**	**5.4E-03**	**1.6E-03**	**7.9E-03**	**3.8E-03**	**1.2E-03**	**7.9E-03**	**4.3E-03**
10	7.6E-04	5.0E-04	1.5E-03	4.6E-04	8.4E-04	1.1E-03	6.7E-04	1.5E-03	1.1E-03

Table Se-2. *Best estimate K_d values (m^3/kg) of selenium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.3E-03**	**7.0E-04**	**2.6E-03**	**6.0E-04**	**3.4E-03**	**2.6E-03**	**4.9E-04**	**4.0E-03**	**3.0E-03**
10	1.2E-03	2.8E-04	4.1E-04	2.2E-04	1.4E-04	3.5E-04	2.8E-04	4.1E-04	3.5E-04

Table Se-3. *Best estimate K_d values (m^3/kg) of selenium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.0E-04**	**6.0E-04**	**9.2E-04**	**3.2E-04**	**1.2E-03**	**5.7E-04**	**4.5E-04**	**1.4E-03**	**6.4E-04**
10	3.1E-04	1.5E-04	2.2E-04	1.2E-04	6.8E-05	1.8E-04	2.3E-04	2.2E-04	1.8E-04

Table Se-4. *Best estimate K_d values (m^3/kg) of selenium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.4E-04**	**1.2E-04**	**2.0E-04**	**1.2E-04**	**8.8E-04**	**2.7E-04**	**1.9E-04**	**2.6E-04**	**3.0E-04**
10	9.7E-05	6.1E-05	1.0E-04	5.1E-05	3.6E-05	8.8E-05	1.4E-04	1.0E-04	8.8E-05

12.2.3 Lower limit K_d values

The lower limit K_d values can be calculated for the rocks by dividing the best estimate values by the uncertainty factors calculated for each rock type. These factors are shown in Table Se-5 and the lower limit K_d values in Tables Se-6 – Se-9.

Table Se-5. *The uncertainty factors for rocks. T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

Reference rock	Factor for random error calculation
T-MGN, P-TGG	5
T-TGG	20*
PGR	50*
*error propagation using the errors in the mica contents and BET/N_2 (surface area) of micas and crushed rock yield unrealistically low correction factor for T-MGN and PGR. Omitting the error in BET/N_2 of crushed rock, the factor for T-TGG is 7 and for PGR 43.	

Table Se-6. *Lower limit K_d values (m^3/kg) of selenium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.5E-03**	**3.6E-04**	**1.1E-03**	**3.2E-03**	**1.6E-03**	**7.6E-04**	**2.4E-04**	**1.6E-03**	**8.6E-04**
10	1.5E-04	1.0E-04	3.0E-04	9.2E-05	1.7E-04	2.2E-04	1.3E-04	3.0E-04	2.2E-04

Table Se-7. *Lower limit K_d values (m^3/kg) of selenium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.6E-04**	**1.4E-04**	**5.2E-04**	**1.2E-04**	**6.8E-04**	**5.2E-04**	**9.8E-05**	**8.0E-04**	**6.0E-04**
10	2.4E-04	5.6E-05	8.2E-05	4.4E-05	2.8E-05	7.0E-05	5.6E-05	8.2E-05	7.0E-05

Table Se-8. *Lower limit K_d values (m^3/kg) of selenium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.0E-05**	**3.0E-04**	**4.6E-05**	**1.6E-05**	**6.0E-05**	**2.9E-05**	**2.3E-05**	**7.0E-05**	**3.2E-05**
10	1.6E-05	7.5E-06	1.1E-05	6.0E-06	3.4E-06	9.0E-06	1.2E-05	1.1E-05	9.0E-06

Table Se-9. *Lower limit K_d values (m^3/kg) of selenium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.8E-06**	**2.8E-06**	**4.0E-06**	**2.4E-06**	**1.8E-05**	**5.4E-06**	**3.8E-06**	**5.2E-06**	**6.0E-06**
10	1.9E-06	1.2E-06	2.0E-06	1.0E-06	7.2E-07	1.8E-06	2.8E-06	2.0E-06	1.8E-06

Since no best estimate K_d value for Se as selenide in reducing conditions is given, in reducing groundwaters for HSe^- a lower limit K_d value of 0 m^3/kg is suggested for all rocks.

12.3 Sorption on clays

12.3.1 Source data

Sorption of Se was determined by a batch method for kaolinite KGa-1b, illite IMt-1 and chlorite CCa-2 (ripidolite) in anoxic OLGA, ALLMR, OLBA and OLSR reference waters (Methodology described in Appendix 4). The R_d values are indicated in Figures Se-16 to Se-20.

In the experiments, the selenium tracer was added as selenite. The speciation of selenium was not determined after the experiment. Since selenate sorption is lower in competition with selenite, we do not, at least, overestimate the sorption of selenium.

Sorption of selenite on Silver Hill illite and smectite in a $NaClO_4$ solution showed a decrease with an increase of pH (Missana et al. 2009). For smectite, the R_d at pH 9 was about half of that at pH 6. For the illite, the decrease of R_d with increase of pH was smaller.

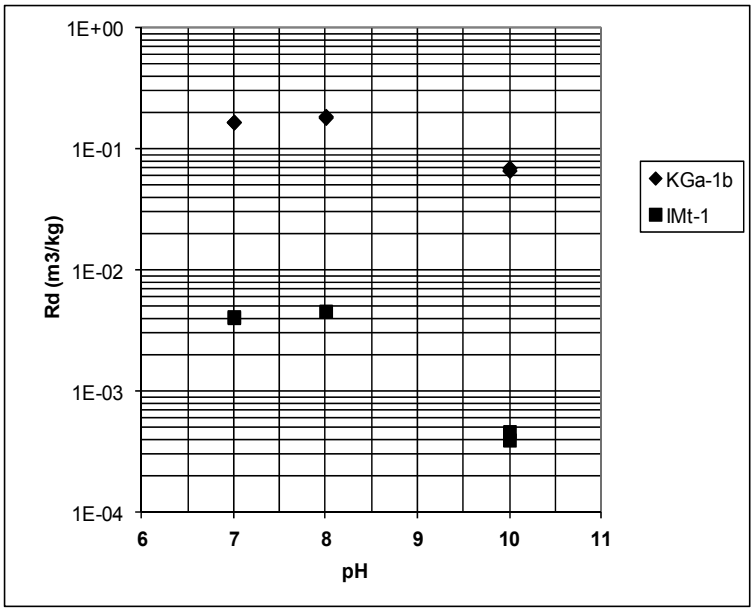

Figure Se-16. *R_d values (m^3/kg) of Se for KGa-1b kaolinite and IMt-1 illite in anoxic glacial meltwater OLGA.*

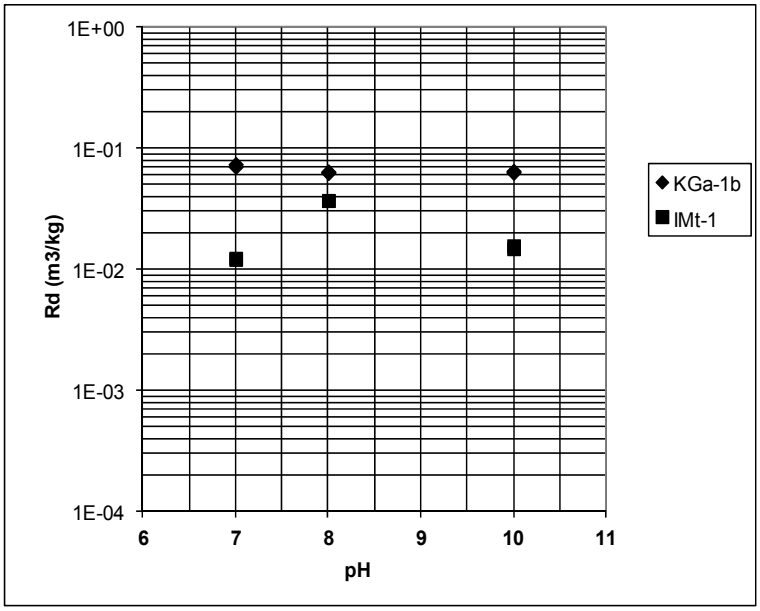

Figure Se-17. *R_d values (m^3/kg) of Se for KGa-1b kaolinite and IMt-1 illite in anoxic fresh ALLMR reference waters.*

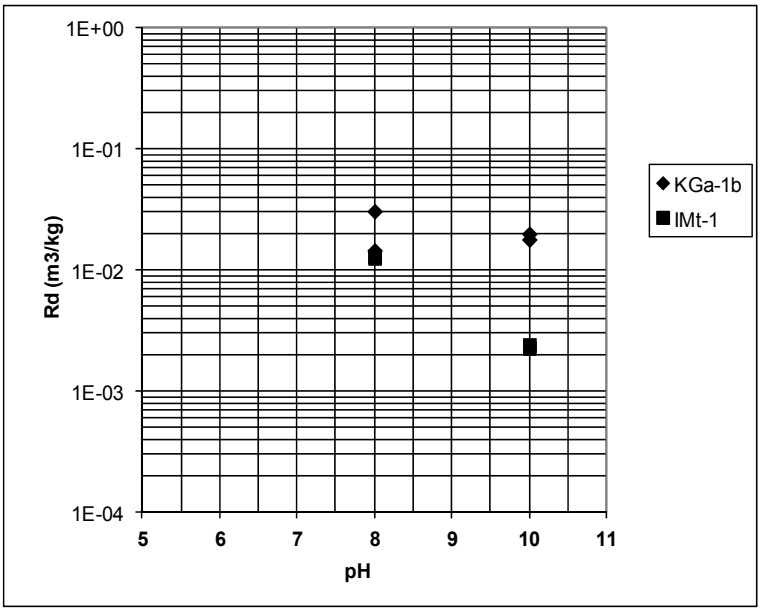

Figure Se-18. *R_d (m^3/kg) values of Se for KGa-1b kaolinite and IMt-1 illite in anoxic brackish OLBA reference waters.*

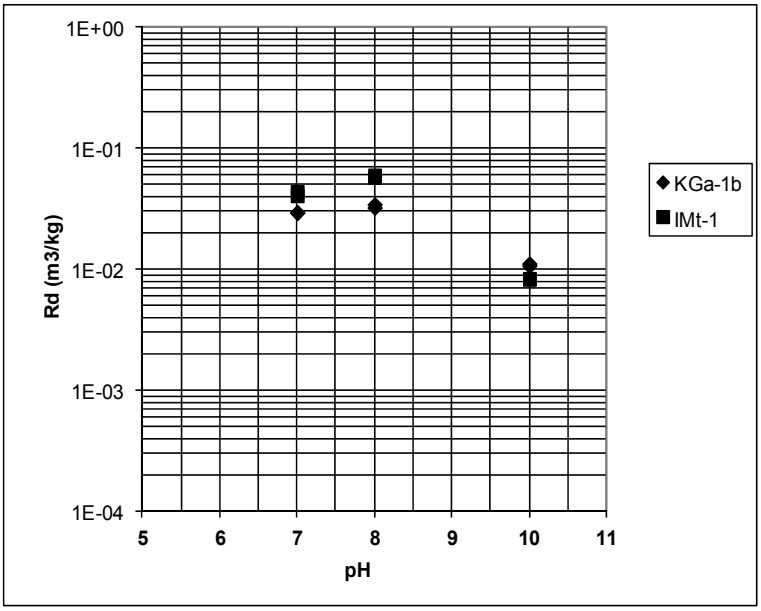

Figure Se-19. *R_d (m^3/kg) values of Se for KGa-1b kaolinite and IMt-1 illite in anoxic saline OLSR reference waters.*

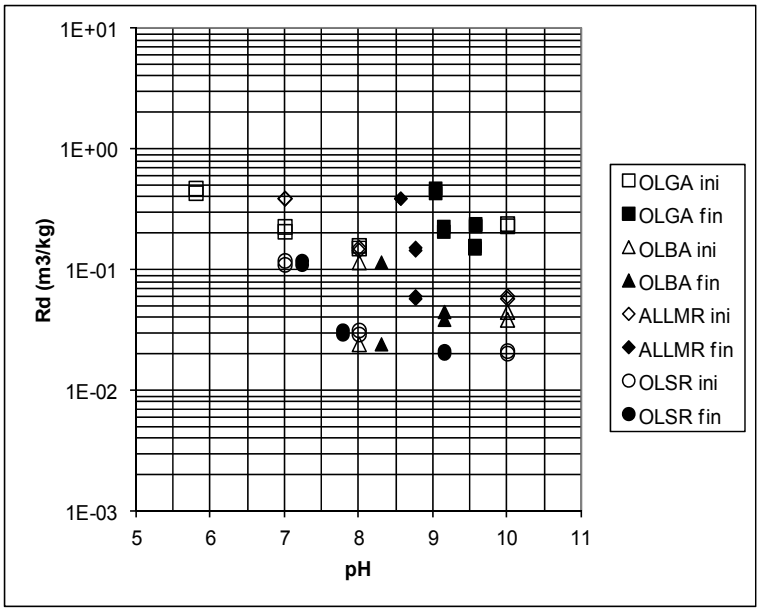

Figure Se-20. *R_d (m^3/kg) values of Se for CCa-2 chlorite (ripidolite) in anoxic reference waters.*

12.3.2 Best estimate K_d values

For clays, kaolinite, illite and chlorite at Olkiluoto, the best estimate values in anoxic waters are given in Tables Se-10 – Se-12. Decrease of sorption with increasing pH is expected. In cases when a higher R_d value was determined for higher pH, the value for the lower pH was chosen, for example for illite in fresh ALLMR reference water at pH 7 and pH 8, the value at pH 7 was chosen for pH 8.

The speciation of Se in brackish KR4_81_1 and saline KR20_465_1 groundwaters is similar to that in fresh ALLMR and saline OLSR reference waters respectively, since the selenium speciation is not sensitive to carbonate concentration. The best estimate K_d values are taken to be the same as in the corresponding reference water (Tables Se-10 – Se-12).

For the clays, the authors only have experimental R_d values under anoxic conditions. In these experiments, the chemical form of Se was most probably selenite. Under oxic conditions in glacial meltwater OLGO and fresh ALLMO reference water, the chemical form may be selenate. For the reference rocks, the R_d values under oxic conditions were about half of the values under anoxic conditions. The K_d values of Se for the clays under oxic conditions are proposed to be one half of the values in anoxic conditions.

Table Se-10. *Best estimate K_d values (m^3/kg) of selenium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.7E-01**	**8.5E-02**	**6.3E-02**	**3.2E-02**	**1.5E-02**	**2.6E-02**	**1.3E-02**	**6.3E-02**	**2.6E-02**
10	6.6E-02	3.3E-02	6.3E-02	3.2E-02	1.5E-02	1.1E-02	5.5E-03	6.3E-02	1.1E-02

Table Se-11. *Best estimate K_d values (m^3/kg) of selenium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.0E-03**	**2.0E-03**	**1.2E-02**	**6.0E-03**	**1.3E-02**	**3.6E-02**	**1.8E-02**	**1.2E-02**	**3.6E-02**
10	4.0E-04	2.0E-04	1.2E-02	6.0E-03	2.3E-03	8.3E-03	4.2E-03	1.2E-02	8.3E-03

Table Se-12. *Best estimate K_d values (m^3/kg) of selenium for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Chlorite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.5E-01**	**7.5E-02**	**1.5E-01**	**7.5E-02**	**2.4E-02**	**2.1E-02**	**1.1E-02**	**1.5E-01**	**2.1E-02**
10	1.5E-01	7.5E-02	3.1E-02	1.6E-02	2.4E-02	2.1E-02	1.1E-02	3.1E-02	2.1E-02

12.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays at Olkiluoto is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab\_field} \quad \text{(Se-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Se-2)}$$

Kaolinite

UF_{source} varies from 1 to 1.2. Deviation in each best estimate K_d value is included in the uncertainty factor UF_{source}.

UF_{model} = 1. No model was used.

UF_{CEC} = 1. The sorption mechanism is assumed to be surface complexation. Since the source data were performed in well-crystallised kaolinite KGa-1b, there is no need for a

Table Se-13. *The uncertainty factors (UF) of Se for kaolinite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{spec}	UF_{pH}	$UF_{Lab\ field}$	UF_{tot}
OLGA	5.8	1	1	1	2	2.1
	10	1	1.4	1	2	2.8
OLGO	-	1	2	1	2	4
ALLMR	8.8	1	1	1	2	2
	10	1	1.4	1	2	2.8
ALLMO	-	1	2	1	2	4
OLBA	7.6	1	1	1	2	2.1
	10	1	1.4	1	2	2.9
OLSR	8.3	1.2	1	2.26	2	5.3
	10	1	1.4	2.26	2	6.6
OLSO	7.2	1.2	1.4	1	2	3.4
	10	1	1.4	2.26	2	6.3
KR4	-	1	2	1	2	4
KR20	7.4	1.2	1.4	2.26	2	7.4
	10	1	1.4	2.26	2	6.6

correction factor concerning differences between the source data and reference conditions. Well-crystallised kaolinite is assumed to sorb selenium oxoanion in equal amounts or less compared with Olkiluoto kaolinite.

UF_{spec} varies from 1 to 2. For the clays, only experimental values under anoxic conditions were available. In these experiments, the chemical form of Se was most probably selenite. Under oxic conditions in glacial meltwater OLGO and fresh ALLMO reference water, the chemical form may be selenate. For the reference rocks, the R_d values under oxic conditions were about half of the values under anoxic conditions. UF_{spec} for these waters is taken as 2. The speciation of Se in brackish KR4_81_1 and saline KR20_465_1 groundwaters is the same as in fresh ALLMR and saline OLSR reference waters respectively. UF_{spec} in these cases is taken as 1.

UF_{pH} varies from 1 to 2.26. A significant pH dependency on K_d values was observed in the source data at a pH range of 8 to 9. In this region, when the reference water was different from the source water, the deviation in K_d values from 0.2 pH unit was taken into account in the uncertainty factor UF_{pH}. Below pH 8 and at pH 10 no pH correction was taken into account in the best estimate K_d values.

UF_{lab_field} =2. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 2 to 7.4.

The uncertainty factors are collected in Table Se-13. Only those factors which are greater than one are listed.

The lower limit K_d values for kaolinite at Olkiluoto are presented in Table Se-16.

Illite

UF_{source} varies from 1 to 1.6. For illite at Olkiluoto, the uncertainty factors are almost the same as for kaolinite. For the waters for which the source R_d data for illite was more scattered than for kaolinite, there is higher uncertainty in the source data, and larger UF_{source} values are used.

UF_{CEC} = 1.3 There is an uncertainty in the CEC values of the IMt-1 illite compared with the Olkiluoto site illite.

UF_{tot} varies from 2.6 to 13.

The uncertainty factors are collected in Table Se-14. Only those factors which are greater than one are listed.

The lower limit K_d values for illite at Olkiluoto are presented in Table Se-17.

Table Se-14. *The uncertainty factors (UF) of Se for illite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{cec}	UF_{spec}	UF_{pH}	UF_{Lab_field}	UF_{tot}
OLGA	5.8	1	1.3	1	1	2	2.6
	10	1	1.3	1.4	2.26	2	8.2
OLGO	-	1	1.3	2	1	2	5.2
ALLMR	-	1	1.3	1.4	1	2	3.6
ALLMO	-	1	1.3	2	1	2	5.2
OLBA	7.6	1	1.3	1	1	2	2.6
	10	1	1.3	1.4	1	2	3.7
OLSR	8.3	1.6	1.3	1.4	2.26	2	13
	10	1	1.3	1.4	2.26	2	8.3
OLSO	7.2	1.6	1.3	1.4	1	2	5.8
	10	1	1.3	1.4	2.26	2	8.2
KR4	-	1	1.3	2	1	2	5.2
KR20	7.4	1.6	1.3	1.4	2.26	2	13
	10	1	1.3	1.4	2.26	2	8.3

Table Se-15. *The uncertainty factors (UF) of Se for chlorite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{cec}	UF_{spec}	UF_{pH}	UF_{Lab_field}	UF_{tot}
OLGA	5.8	1	1.3	1.4	1	2	3.6
	10	1	1.3	1	2.26	2	5.9
OLGO	-	1	1.3	2	1	2	5.2
ALLMR	8.8	1	1.3	1	1	2	2.6
	10	1	1.3	1.4	1	2	3.6
ALLMO	-	1	1.3	2	1	2	5.2
OLBA	7.6	1	1.3	1	1	2	2.6
	10	1	1.3	1.4	1	2	3.7
OLSR	8.3	1.6	1.3	1	2.26	2	9.4
	10	1	1.3	1.4	2.26	2	8.3
OLSO	7.2	1.6	1.3	1.4	1	2	5.8
	10	1	1.3	1.4	2.26	2	8.2
KR4	-	1	1.3	2	1	2	5.2
KR20	7.4	1.6	1.3	1.4	2.26	2	13
	10	1	1.3	1.4	2.26	2	8.3

Chlorite

For chlorite, the uncertainty factors are used as for illite: only minor differences in the uncertainties are observed.

UF_{source} varies from 1 to 1.6. For chlorite at Olkiluoto, the uncertainty factors are almost the same as for kaolinite and illite.

UF_{CEC} = 1.3 There is an uncertainty in the CEC values for the CCa-2 chlorite compared with the Olkiluoto site chlorite.

UF_{tot} varies from 2.6 to 13.

The uncertainty factors are collected in Table Se-15. Only those factors which are greater than one are listed.

The lower limit K_d values for chlorite at Olkiluoto are presented in Table Se-18.

Table Se-16. *Lower limit K_d values (m^3/kg) of selenium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**8.3E-02**	**2.1E-02**	**3.1E-02**	**8.0E-03**	**7.0E-03**	**4.9E-03**	**3.8E-03**	**1.6E-02**	**3.5E-03**
10	2.4E-02	8.3E-03	2.2E-02	8.0E-03	5.2E-03	1.7E-03	8.7E-04	1.6E-02	1.7E-03

Table Se-17. *Lower limit K_d values (m^3/kg) of selenium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.5E-03**	**3.8E-04**	**3.3E-03**	**1.2E-03**	**5.0E-03**	**2.7E-03**	**3.1E-03**	**2.3E-03**	**2.7E-03**
10	4.9E-05	3.8E-05	3.3E-03	1.2E-03	6.2E-04	1.0E-03	5.1E-04	2.3E-03	1.0E-03

Table Se-18. *Lower limit K_d values (m^3/kg) of selenium for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Chlorite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.1E-02**	**1.4E-02**	**5.8E-02**	**1.4E-02**	**9.2E-03**	**2.2E-03**	**1.9E-03**	**2.9E-02**	**1.6E-03**
10	2.6E-02	1.4E-02	8.5E-03	3.1E-03	6.5E-03	2.5E-03	1.3E-03	6.0E-03	2.5E-03

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13 MOLYBDENUM

13.1 Speciation

The speciation of molybdenum was calculated with the PHREEQC programme using the Thermo_Chimie database Version 7b (ANDRA 2009). Molybdenum exists as a solute in the form of the molybdate ion, MoO_4^{2-}, in the pH and redox conditions of the rock-groundwater conditions, as exemplified in Figure Mo-1 for granitic groundwater ALLMR. In sulphidic waters, sulphidisation of MoO_4^{2-} to MoS_4^{2-} is possible and the MoS_4^{2-} would be soluble. At pH 8.3 the HS^-activity concentration should be higher than $10^{-3.6}$ M for sulphidisation of $MoO4^{2-}$ (Helz et al. 1996). The measured sulphide concentration in the Olkiluoto groundwaters has been this high only in the brackish KR13_362_4 water, making this reaction unlikely in the reference waters (Hellä et al. 2014). In nature, the sulphidisation of MoO_4^{2-} in seas is followed by scavenging of Mo to sediments. In this report, Mo is assumed to exist solely as MoO_4^{2-} in the groundwaters.

The molybdate ion is not complexed in groundwater conditions. Molybdate is precipitated in neutral to slightly basic conditions by calcium when an acidic solution is neutralised. The solubility of fresh, finely crystalline $CaMoO_4 \cdot 0.5\ H_2O$ in deionised water is $3 \cdot 10^{-4}$ M, giving a solubility product of $9 \cdot 10^{-8}$ mol^2 .

The solubility of molybdenum in the groundwaters considered in this report is assumed to be limited by $CaMoO_4 \cdot 0.5\ H_2O$ as an analogue to the solubility limitation of selenate. The estimated solubility of molybdenum is $5 \cdot 10^{-4}$ mol/L in the fresh ALLMR type groundwater under aerobic conditions. In glacial melt water OLGA, the solubility is higher owing to low Ca concentration. Solubility of MoS_2, the most important molybdenum ore mineral, is lower but due to its hydrothermal origin it is not precipitated in low temperature bedrock conditions (Bostick et al. 2000). Under reducing conditions, the solubility was calculated to be controlled by the solubility of MoO_2 and the solubility is $(8–70) \cdot 10^{-8}$ M (Grive et al. 2008).

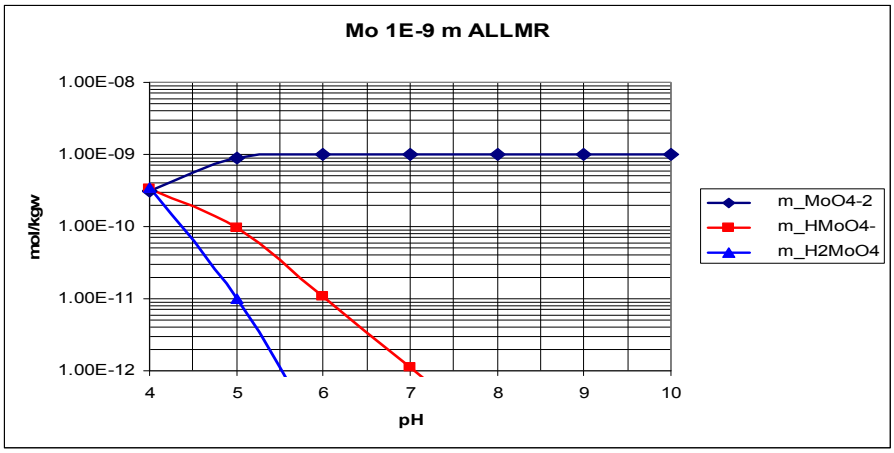

Figure Mo-1. *Speciation of molybdenum in fresh ALLMR water.*

13.2 Sorption on rocks

Quantitative results of sorption of molybdate on silicate minerals are sparse.

The LFER (linear free energy relationship) method has been used for the estimation of the ferric oxide surface complexation constants of molybdate from the values of other oxyanions (Dzombak & Morel 1990). The estimated values show that the pH dependent sorption edge for molybdate lies between the edges for chromate and vanadate (Stumm & Morgan 1996). This estimation is in agreement with the measured sorption on aluminium oxide. Sorption of molybdate on ferric oxides and kaolinite is probable in the lowest pH region of the fresh groundwater. It can be estimated that the sorption of molybdenum in bedrock conditions resembles the sorption of other anionic waste elements and other oxyanions.

The anions strongly competing with molybdate in the sorption are arsenate and phosphate ions having ionic charge of -3 (Goldberg et al. 2010, Wu et al. 2001, Xu et al. 2006), but at the trace concentrations, like selenite (SeO_3^{-2}) in the Olkiluoto groundwaters, they do not decrease the sorption of molybdate. The effects of sulphate (ionic charge -2) are much less, even at higher concentrations. Sorption of molybdate on soils is only marginally decreased from sorption in typical low salinity water (ALLMR) to medium saline (OLBA) groundwater (Goldberg et al. 2009).

13.2.1 Source data

Batch sorption experiments were performed for the crushed Olkiluoto rocks in fresh ALLMR and saline OLSR reference waters. The rocks were P series granodiorite gneiss (P-TGG), T series granodiorite gneiss (T-TGG) and pegmatite granite (PGR). The chosen rocks had different mica contents. The sorption data of Mo on P-TGG, T-TGG and PGR is presented in Figures Mo-2, Mo-3 and Mo-4. The experimental method is described in Appendix 4. The pH was varied in order to obtain experimental results for the pH dependency of sorption. The R_d values for the rocks presented in Figures Mo-2 – Mo-4 indicate that sorption in the saline water is lower than in the fresh water, and that sorption decreases with increasing pH more rapidly on the rocks with low mica content.

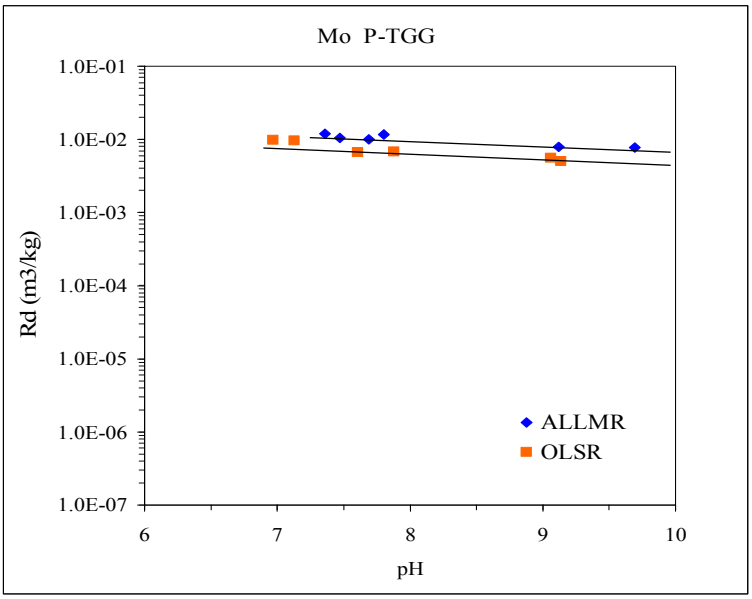

Figure Mo-2. *R_d values (m^3/kg) of Mo for crushed P-TGG gneiss in fresh ALLMR and saline OLSR reference waters.*

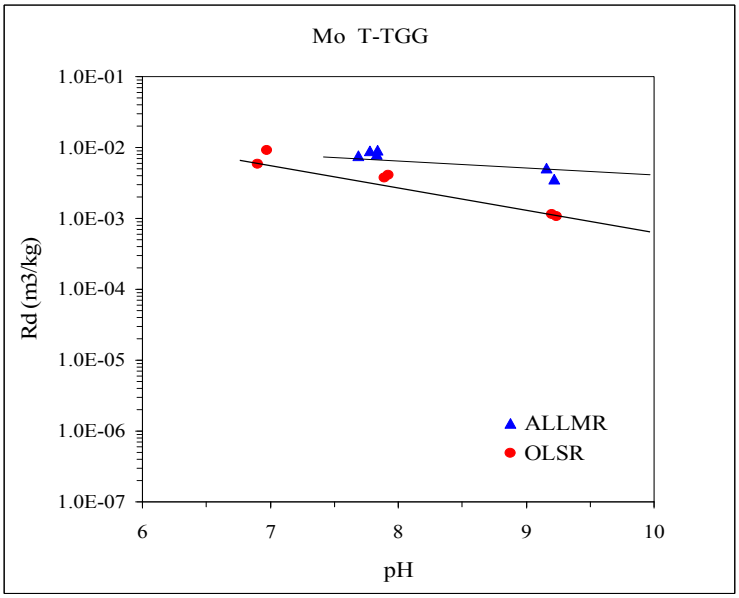

Figure Mo-3. *R_d values (m^3/kg) of Mo for crushed T-TGG gneiss in fresh ALLMR and saline OLSR reference waters.*

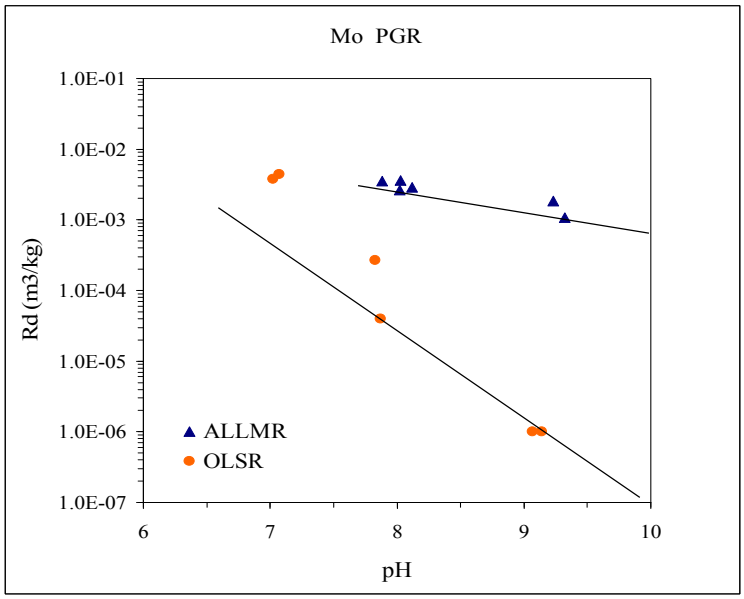

Figure Mo-4. *R_d values (m^3/kg) of Mo for crushed PGR granite in fresh ALLMR and saline OLSR reference waters.*

13.2.2 Best estimate K_d values

The K_d values of molybdenum were converted from the experimental R_d values of Mo with the following method. A straight line was fitted to the experimental results so that the line presented the decrease of R_d values as the pH increased. The R_d values were calculated with the help of the line in the range of experimental pH values. The R_d value at pH 10 was estimated from the R_d value at pH 9. The factors for converting the R_d values to K_d values of intact rock are given in Chapter 3 (Derivation of K_d for intact rocks and clays).

The best estimate K_d values of molybdenum for the rocks T-MGN, P-TGG, T-TGG and PGR are presented in Tables Mo-1, Mo-2, Mo-3 and Mo-4. The experimental R_d values were for the rocks P-TGG, T-TGG and PGR in ALLMR and OLSR waters.

Lower R_d values in saline OLSR than in fresh ALLMR waters are expected to be due to competition between molybdate ion and anions in these waters.

The K_d values of OLGA and OLGO waters (glacial melt water) were calculated from the R_d values of fresh ALLMR water. The K_d values of carbonate-containing reducing brackish water OLBA were calculated from the R_d values of saline OLSR water. The K_d values of oxic waters ALLMO and OLSO were the same as the values of the corresponding anoxic waters ALLMR and OLSR respectively. The K_d values of brackish KR4_81_1 water were the same as ALLMR water and the K_d values of saline KR20_465_1 water were the same as those of OLSR water.

Table Mo-1. *The best estimate K_d (m^3/kg) values of molybdenum for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.6E-03**	**2.6E-03**	**2.0E-03**	**1.5E-03**	**1.4E-03**	**2.4E-03**	**2.3E-03**
10	1.6E-03	1.6E-03	1.6E-03	9.2E-04	9.2E-04	9.2E-04	9.2E-04

Table Mo-2. *The best estimate K_d (m^3/kg) values for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.3E-03**	**1.3E-03**	**1.0E-03**	**8.0E-04**	**7.0E-04**	**1.2E-03**	**8.0E-04**
10	0.8E-03	0.8E-03	0.8E-03	4.4E-04	4.4E-04	4.4E-04	4.4E-04

Table Mo-3. *The best estimate K_d (m^3/kg) values of molybdenum for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.6E-04**	**8.6E-04**	**5.0E-04**	**5.0E-04**	**3.6E-04**	**7.2E-04**	**5.4E-04**
10	2.4E-04	2.4E-04	2.4E-04	1.0E-05	1.0E-05	1.0E-05	1.0E-05

Table Mo-4. *The best estimate K_d (m^3/kg) values of molybdenum for pegmatitic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1*
KR20 = KR20_465_1.

pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.7E-04**	**1.7E-04**	**7.7E-05**	**3.4E-06**	**2.4E-06**	**1.3E-04**	**4.1E-06**
10	9.4E-06	9.4E-06	9.4E-06	4.7E-07	4.7E-07	4.7E-07	4.7E-07

13.2.3 Lower limit K_d values

The lower limit K_d values were calculated by dividing the best estimate value by an uncertainty factor. The lower limit values of the T-MGN, P-TGG, T-TGG and PGR rocks are presented in Tables Mo-6 – Mo-9.

The uncertainty of the measured R_d values of the Olkiluoto rocks T-MGN, P-TGG, T-TGG and PGR was small compared with the uncertainty of the R_d to K_d conversion factor. The uncertainty factors for the rocks are presented in Table Mo-5.

Table Mo-5. *The uncertainty factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	5
P-TGG	5
T-TGG	20
PGR	50

Table Mo-6. *The lower limit K_d (m^3/kg) values of molybdenum for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.2E-04**	**5.2E-04**	**4.0E-04**	**3.0E-04**	**2.8E-04**	**4.8E-04**	**4.6E-04**
10	3.2E-04	3.2E-04	3.2E-04	1.8E-04	1.8E-04	1.8E-04	1.8E-04

Table Mo-7. *The lower limit K_d (m^3/kg) values of molybdenum for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.6E-04**	**2.6E-04**	**2.0E-04**	**1.6E-04**	**1.4E-04**	**2.4E-04**	**1.6E-04**
10	1.6E-04	1.6E-04	1.6E-04	8.8E-05	8.8E-05	8.8E-05	8.8E-05

Table Mo-8. *The lower limit K_d (m^3/kg) values of molybdenum for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.3E-05**	**4.3E-05**	**2.5E-05**	**2.5E-05**	**1.8E-05**	**3.6E-05**	**2.7E-05**
10	1.2E-05	1.2E-05	1.2E-05	5.0E-07	5.0E-07	5.0E-07	5.0E-07

Table Mo-9. *The lower limit K_d (m^3/kg) values of molybdenum for pegmatitic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.4E-06**	**3.4E-06**	**1.5E-06**	**6.8E-08**	**4.8E-08**	**2.6E-06**	**8.2E-08**
10	1.9E-07	1.9E-07	1.9E-07	9.4E-09	9.4E-09	9.4E-09	9.4E-09

13.3 Sorption on clays

13.3.1 Source data

Sorption experiments on molybdenum on clays were performed in fresh reducing ALLMR and saline reducing OLSR reference waters. The clays were a well-crystallised kaolinite KGa-1b and illite IMt-1 (Clay Mineral Society). The sorption of Mo on clays KGa-1b and IMt-1 is presented in Figures Mo-5 and Mo-6. The decrease of sorption with the increase of pH was observable.

Due to its importance to plants, the behaviour of molybdenum has been studied in soils and clays. Sorption on kaolinite and illite in 0.1 M NaCl at pH 2–12 is given in Goldberg et al. (1996). Only approximate K_d values could be derived from the graphs of illite. The K_d value for illite at pH 6 was $4 \cdot 10^{-3}$ m^3/kg and decreased to $6 \cdot 10^{-4}$ m^3/kg at pH 10. Single-pH sorption isotherms of Mo for kaolinite, illite and montmorillonite are given in Motta & Miranda (1989). The K_d values in 0.01 M NaCl at the linear part of the isotherms were derived from the graphs and were $1.3 \cdot 10^{-1}$ m^3/kg for kaolinite at pH 4.6 to 5.5, $6 \cdot 10^{-3}$ m^3/kg for illite at pH 8.9 and $3 \cdot 10^{-1}$ m^3/kg for montmorillonite at pH 3.98–4.04. The values derived from Motta & Miranda (1986) are in fair agreement with the values in Figures Mo-5 and Mo-6.

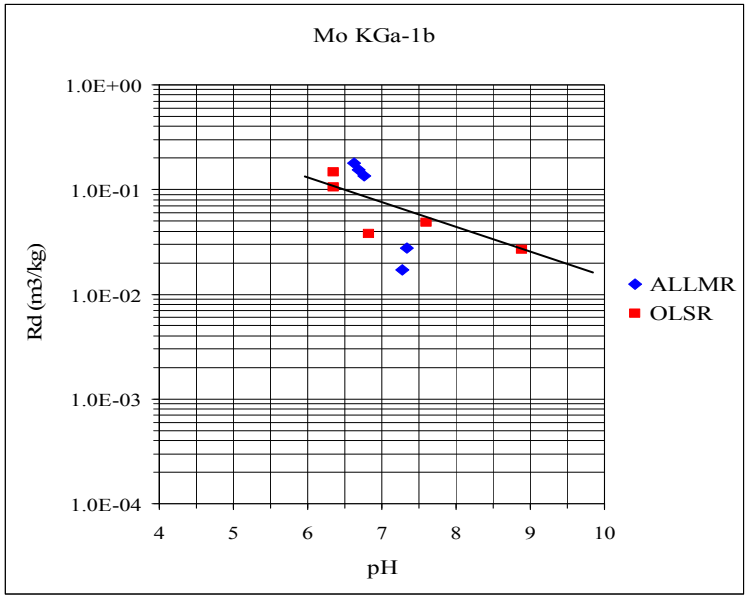

Figure Mo-5. *R_d values (m^3/kg) of Mo for kaolinite KGa-1b in fresh ALLMR and saline OLSR reference waters.*

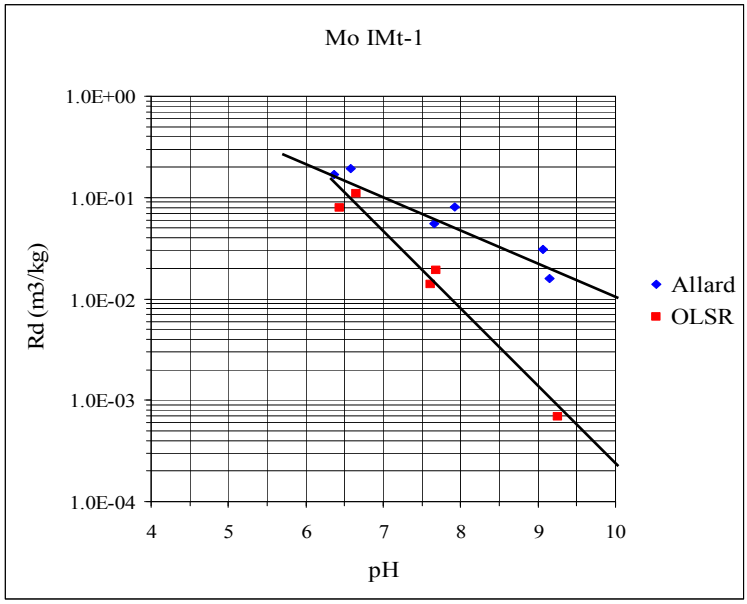

Figure Mo-6. *R_d values (m^3/kg) of Mo for illite IMt-1 in fresh ALLMR and saline OLSR reference waters.*

13.3.2 Best estimate K_d values

The best estimate values of molybdenum for kaolinite and illite in the Olkiluoto geosphere are presented in Tables Mo-10 and Mo-11.

There are only a few experimental data points of sorption on kaolinite in fresh ALLMR water. As shown with illite, sorption in the saline water was the same or lower than in the fresh water. As a conservative measure, the data points for sorption in the saline OLSR water were used to get the best estimate values for the reference waters. A line was fitted to the R_d values of OLSR and the K_d values for the reference waters were calculated from R_d value at the pH of the water.

The K_d values for illite IMt-1 were derived using lines fitted to the R_d values of the ALLMR and OLSR waters. The speciation of molybdenum is the same in all reference waters and no correction is needed for this. Values for glacial water and KR4_81_1 were derived from sorption data in ALLMR water and for the other reference waters from sorption in OLSR water.

Table Mo-10. *The best estimate K_d (m^3/kg) values of molybdenum for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E-01**	**1.0E-01**	**2.9E-02**	**6.6E-02**	**4.5E-02**	**2.7E-02**	**2.7E-02**
10	1.5E-02	1.5E-02	1.5E-02	1.5E-02	1.5E-02	1.5E-02	1.5E-02

Table Mo-11. *The best estimate K_d (m^3/kg) values of molybdenum for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.7E-01**	**1.7E-01**	**3.4E-02**	**1.5E-02**	**5.0E-03**	**5.0E-02**	**2.8E-02**
10	1.0E-02	1.0E-02	1.0E-02	1.8E-04	1.8E-04	1.0E-02	1.8E-04

13.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(Mo-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Mo-2)}$$

The uncertainty factors are collected in Tables Mo-13, Mo-14. Only those factors which are greater than one are listed.

Kaolinite

UF_{tot}= 12 (2 * 1 * 1 * 1.4 * 2.1 * 2) the total uncertainty factor for the reference waters except OLSR.

UF_{tot}= 6 (2 * 1 * 1 * 1 * 1.5 * 2) for OLSR water.

UF_{source}= 2. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for kaolinite were calculated. The factor 2 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1. Cation exchange capacity was not relevant here and so the factor is 1.

UF_{spec}= 1 the uncertainty of speciation factor for OLSR water. The best estimate K_d values for kaolinite KGa-1b were calculated from the experimental R_d values of OLSR.

UF_{spec}= 1.4 for other reference waters as proposed in Hummel & Berner (2002).

UF_{pH}= 1.5. The uncertainty of pH on the R_d values for OLSR water.

UF_{pH}= 2.1 for other reference waters.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Mo for kaolinite in the Olkiluoto geosphere is presented in Table Mo-12.

Illite

UF_{tot}= 15 (2 * 1 * 1.3 * 1.4 * 2.1 * 2) the total uncertainty factor for the reference waters except for ALLMR and OLSR.

UF_{tot}= 8 for ALLMR and OLSR waters.

UF_{source}= 2. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for kaolinite were calculated. The factor 2 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity (UF_{CEC}) covers the differences between the IMt-1 illite and natural illites (Bradbury & Baeyens 2003, Missana et al. 2008).

UF_{spec}= 1 the uncertainty of speciation factor for ALLMR and OLSR waters as the best estimate K_d values for illite were calculated from the experimental R_d values of ALLMR and OLSR waters.

Table Mo-12. *The lower limit K_d (m^3/kg) values of molybdenum for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.3E-03**	**8.3E-03**	**2.4E-03**	**5.5E-03**	**7.5E-03**	**2.3E-03**	**2.3E-03**
10	1.3E-03	1.3E-03	1.3E-03	1.3E-03	2.5E-03	1.3E-03	1.3E-03

UF_{spec}= 1.4 for other reference waters as proposed in Hummel and Berner (2002).

In the case of illite IMt-1, the experimental data for ALLMR and OLSR waters were used. So the uncertainty factor UF_{pH} is 1.5 for ALLMR and OLSR and 2.1 for other reference waters.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Mo for kaolinite in Olkiluoto geosphere is presented in Table Mo-13.

Table Mo-13. *The lower limit K_d (m^3/kg) values of molybdenum for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.1E-02**	**1.1E-02**	**4.3E-03**	**1.0E-03**	**6.3E-04**	**3.3E-03**	**1.9E-03**
10	6.7E-04	6.7E-04	1.3E-03	1.2E-05	2.3E-05	6.7E-04	1.2E-05

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14 TECHNETIUM

14.1 Speciation

Technetium has no stable isotopes and exists in nature as a fission product. Under oxidising conditions, Tc is present in the form of Tc(VII) as the TcO_4^- ion and is highly soluble. TcO_4^- does not form complexes in groundwater.

Under anoxic conditions technetium is at oxidation state IV and forms hydroxo complexes and may form mixed Tc-hydroxocarbonato complexes. The modelling results of Grivé et al. (2008) indicate that the solubility limited concentration of $TcO(OH)_2aq$ under reducing conditions is $(4.2 - 5)\cdot10^{-9}$ M. Speciation calculations made using $1\cdot10^{-9}$ M Tc indicate that the soluble species in reducing solutions is $TcO(OH)_2$ aq and that the impact of carbonato complexation is small, as also is other hydroxo complexation at a pH of interest in this report. At pH 10, the $TcO(OH)_3^-$ comprises about 10% of the total Tc. Figures Tc-1 and Tc-2 indicate the chemical species of Tc(IV) in the low-salinity glacial meltwater OLGA and in the high-carbonate brackish reference water OLBA. Figure Tc-3 shows that, even in the most carbonate-containing groundwater, the impact on Tc(IV) carbonato complexation is minor.

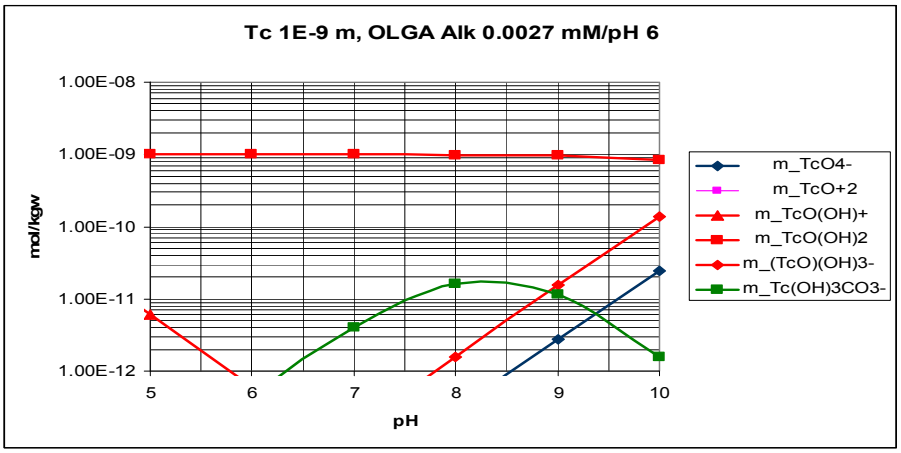

Figure Tc-1. *Speciation of Tc in anoxic glacial meltwater OLGA.*

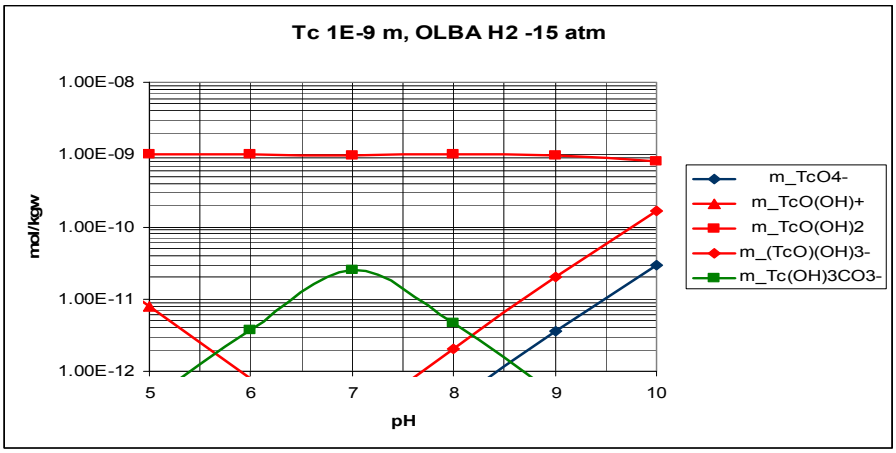

Figure Tc-2. *Speciation of Tc in anoxic brackish reference water OLBA.*

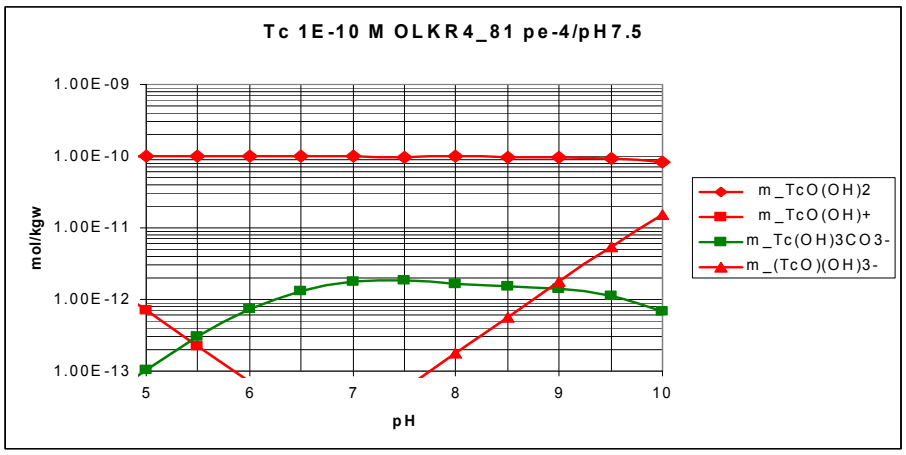

Figure Tc-3. *Speciation of Tc in brackish KR4_81_1 groundwater.*

14.2 Sorption on rocks

14.2.1 Source data

Sorption of Tc(VII) on Olkiluoto mica gneiss and tonalite had R_d values ranging from $2 \cdot 10^{-4}$ m^3/kg to $1 \cdot 10^{-3}$ m^3/kg in the pH range 7-8 on granite (Koskinen et al. 1985). In the same conditions, the sorption of iodide was around the same. The sorption of Tc is reviewed in EPA (2004) and the low sorption of Tc(VII) is confirmed in many publications. Sorption of pertechnetate on mineral solids is low but not zero. As it is an anion, the sorption of TcO_4^- is expected to decrease with an increase of pH.

Under reducing conditions, the sorption of Tc on granitic rocks had R_d values 0.2 m^3/kg to 1 m^3/kg (Hakanen & Lindberg 1995). No data on the sorption of Tc(IV) were found that could be used for defining the best estimate K_d values of Tc(IV) for rocks.

14.2.2 Best estimate K_d values

Oxic conditions

No in-house data or open source information in reference water conditions and for reference rocks are available for technetium. The same best estimate and conservative K_d values as for iodine are recommended (see Chapter 6.2.2).

Anoxic conditions

There are no data on Tc(IV) sorption on silicate minerals under anoxic conditions. The speciation of Tc(IV) indicates that hydroxo complexes dominate in all anoxic reference waters and that Tc(IV) has a lower carbonato complexation tendency than Th. Th is used as a chemical analogue to Tc(IV) and the best estimate K_d values of Tc(IV) are suggested to be the same as for Th (IV) (see Chapter 20.2.2). The fraction of Tc(IV) species in OLGA at pH 10 (0.975 in Figure Tc-1) was taken into account in its K_d values.

The best estimate K_d values for rocks are listed in Tables Tc-1 – Tc-4.

Table Tc-1. *Best estimate K_d values (m^3/kg) of Tc(IV,VII) for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E+00**	**6.0E-04**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**
10	7.8E+00	6.0E-06	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00

Table Tc-2. *Best estimate K_d values (m^3/kg) of Tc(IV,VII) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E+00**	**3.0E-04**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	3.9E+00	3.0E-06	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Tc-3. *Best estimate K_d values (m^3/kg) of Tc(IV,VII) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+00**	**2.0E-04**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	3.9E+00	1.0E-06	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Tc-4. *Best estimate K_d values (m^3/kg) of Tc(IV,VII) for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-01**	**4.0E-05**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**
10	9.8E-01	2.7E-07	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00

14.2.3 Lower limit K_d values

Oxic conditions

No in-house data are available for reference rocks in reference waters, therefore the same lower limit K_d values as for iodine are recommended (see Chapter 6.2.3).

Anoxic conditions

For the same reason as for the best estimate values, the same lower limit K_d values for Tc(IV) as for Th are proposed (see Chapter 20.2.3).

The lower limit K_d values for rocks are listed in Tables Tc-5 – Tc-8.

Table Tc-5. *Lower limit K_d values (m^3/kg) of Tc(IV,VII) for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-01**	**8.6E-05**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**
10	3.9E-01	8.6E-06	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01

Table Tc-6. *Lower limit K_d values (m^3/kg) of Tc(IV,VII) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-02**	**4.3E-05**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	1.5E-07	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Tc-7. *Lower limit K_d values (m^3/kg) of Tc(IV,VII) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E-02**	**1.0E-05**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	5.0E-08	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Tc-8. *Lower limit K_d values (m^3/kg) of Tc(IV,VII) for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**8.0E-07**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**
10	2.0E-02	5.4E-09	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02

14.3 Sorption on clays

14.3.1 Source data

No in-house data are available for reference clays in reference waters.

14.3.2 Best estimate K_d values

Oxic conditions

The best estimate K_d values of Tc(VII) are suggested to be the same as for iodine (see Chapter 6.3.2).

Anoxic conditions

The speciation of Tc(IV) indicates that the hydroxo complexes dominate in all anoxic reference waters and that Tc(IV) has lower carbonato complexation tendency than Th. The best estimate K_d values are suggested to be the same as for Th (IV) (see Chapter 20.3.2).

The best estimate K_d values for clays are listed in Tables Tc-9 – Tc-10.

Table Tc-9. *Best estimate K_d values (m^3/kg) of Tc(IV,VII) for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E+01**	**1.0E-01**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**
10	2.0E+02	1.1E-03	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02

Table Tc-10. *Best estimate K_d values (m^3/kg) of Tc(IV,VII) for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E+01**	**3.6E-03**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**
10	2.0E+01	4.0E-05	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01

14.3.3 Lower limit K_d values

Oxic conditions

The lower limit K_d values of Tc(VII) for clays, kaolinite and illite at Olkiluoto are suggested to be the same as the lower limit K_d values for the I(-I) analogue (see Chapter 6.3.3).

Anoxic conditions

The lower limit K_d values of Tc(IV) for clays, kaolinite and illite at Olkiluoto are suggested to be the same as the lower limit K_d values for the Th (IV) analogue (see Chapter 20.3.3).

The lower limit K_d values for clays are listed in Tables Tc-11 – Tc-12.

Table Tc-11. *Lower limit K_d (m^3/kg) values of Tc(IV,VII) for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E+01**	**6.7E-03**	**8.4E+01**	**8.3E+01**	**8.4E+01**	**6.0E+01**	**6.0E+01**
10	8.2E+01	7.3E-05	8.4E+01	8.4E+01	8.4E+01	6.0E+01	6.0E+01

Table Tc-12. *Lower limit K_d (m^3/kg) values of Tc(IV,VII) for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E+00**	**1.4E-04**	**7.5E+00**	**7.5E+00**	**7.5E+00**	**5.3E+00**	**5.3E+00**
10	7.3E+00	1.5E-06	7.5E+00	7.5E+00	7.5E+00	5.3E+00	5.3E+00

REFERENCES

EPA 2004. Understanding variations in partition coefficient, Kd, values Volume III: Review of Geochemistry and Available Kd Values for Americium, Arsenic, Curium, Iodine, Neptunium, Radium, and Technetium. Environmental Protection Agency, United States Office of Air and Radiation EPA 402-R-04-002C.

Grivé, M., Montoya, V., Duro, L. 2008. Assessment of the concentration limits for radionuclides for Posiva. Posiva Oy, Olkiluoto, Finland, Posiva Working Report 2007-103.

Hakanen, M. & Lindberg, A. 1995. Technetium, neptunium and uranium in simulated anoxic groundwater conditions. Nuclear Waste Commission of Finnish Power Companies, Helsinki, Finland, Report YJT-95-02.

Koskinen, A., Alaluusua, M., Pinnioja, S., Jaakkola, T. 1985. Sorption of iodine, neptunium, technetium, thorium and uranium on rocks and minerals. Nuclear Waste Commission of Finnish Power Companies, Helsinki, Finland, Report YJT-85-36.

15 NIOBIUM

15.1 Speciation

Niobium is present in groundwaters in the oxidation state of V. Niobium forms relatively stable complexes with both fluoride and oxalate ions (Steinberg 1961). At relatively high Nb concentrations (0.05-0.15 M), polynuclear hydroxides are formed, which become soluble in an excess of hydroxide ions. The soluble forms are considered to be anionic (Baes & Mesmer 1986). The formation constants and the existence of the anionic mononuclear $Nb(OH)_6^-$ species (also marked as NbO_3^-) are regarded by Baes & Mesmer (1986) as very approximate. This species is included in many thermodynamical databases (TDB) for the interpretation of the increase of Nb solubility with pH. Calculated speciation of Nb ($1 \cdot 10^{-10}$ M) in Figure Nb-1 using the TDB of Grivé et al. (2008) suggests that in the groundwaters, $Nb(OH)_5$ dominates at pH lower than 7.3. At higher pH, NbO_3^- ($Nb(OH)_6^-$) is the dominating species. According to ANDRA's Thermo_Chimie Version 7b database (ANDRA 2009), the major species are anionic at pH 5 and higher (Figure Nb-2).

In the groundwaters, Nb forms only hydroxo complexes. The calculated speciation is dependent only on pH and is the same in all of the reference groundwaters. In the Olkiluoto groundwaters, the concentration of niobium has not been determined.

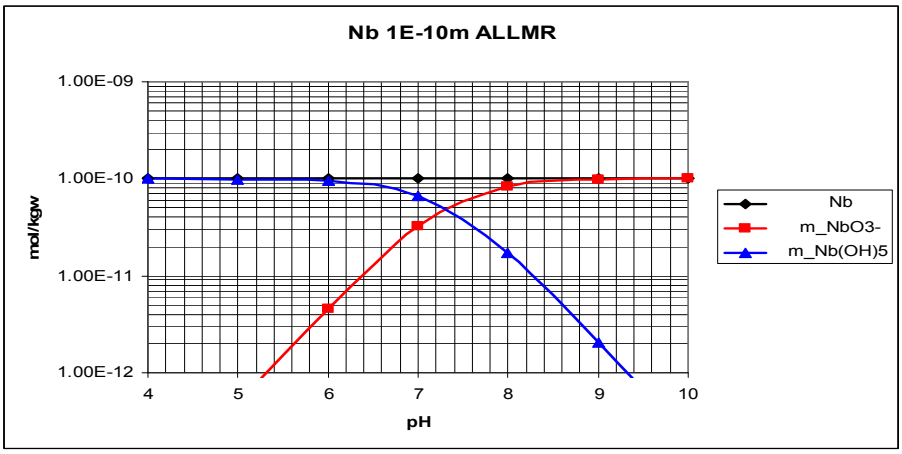

Figure Nb-1. *Speciation of trace concentrations of Nb in fresh reference water ALLMR (TDB from Grivé et al. (2008)).*

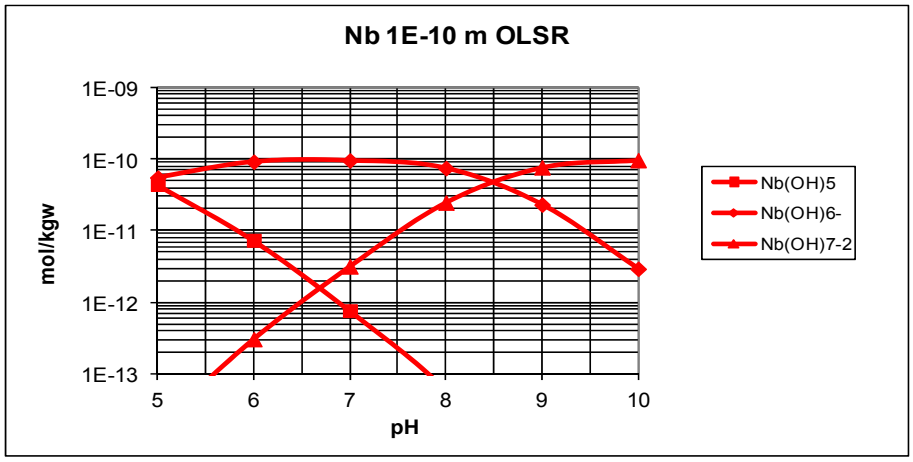

Figure Nb-2. *Speciation of trace concentrations of Nb in saline reference water OLSR (Thermo_Chimie Version 7b TDB from ANDRA (2009)).*

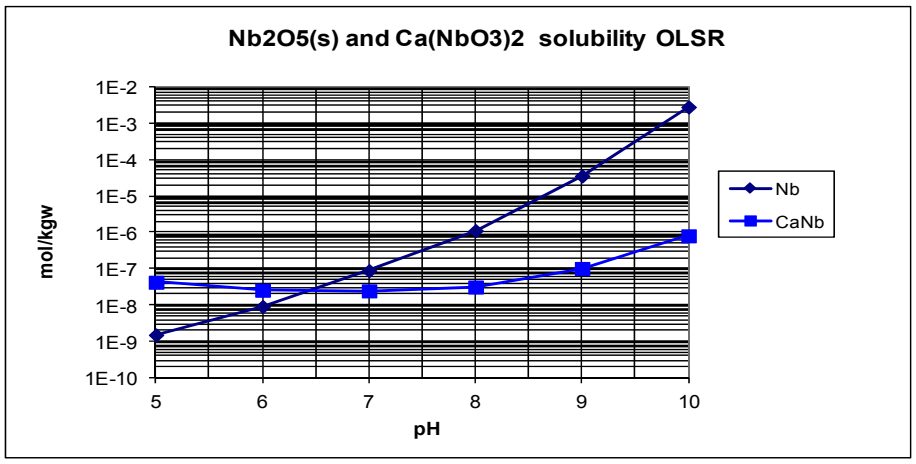

Figure Nb-3. *Solubility of $Ca(NbO_3)_2$(blue) and Nb_2O_5(s)(dark blue) in saline water OLSR.*

Solubility

The solubility of Nb in NaOH solutions oversaturated with Nb(V) was determined by Kulmala & Hakanen (1993). The measured solubilities are in good accordance with the solubilities calculated for groundwater (Bruno et al. 1997) and bentonite water conditions (Berner 1995) and the calculated solubility in NaCl solution using the TDB of Grivé et al. (2008). An undersaturation experiment with Nb_2O_5 solid in cement pore water showed much lower solution concentrations of Nb at pH 13 (Kulmala & Hakanen 1993). The difference between the conditions in the oversaturation and the undersaturation experiments was that only the cement pore water contained calcium ions. There is some evidence that Nb concentration in a cementitious environment is limited by the solubility of $Ca(NbO_3)_2 \cdot H_2O$ (Lothenbach et al. 1999, Talerico et al. 2004). The solubility of $Ca(NbO_3)_2$ in the calcium containing OLSR water was calculated using the value for the solubility product in Sillén (1964) (Figure Nb-3). The

solubility of $Ca(NbO_3)_2$ is higher than that of Nb_2O_5(s), calculated using Thermo_ Chimie Version 7b TDB (ANDRA 2009) (Figure Nb-3) or calculated for Nb_2O_5 (cr) in groundwaters in Grivé et al. (2008).

15.2 Sorption on rocks

Sorption of niobium on the Olkiluoto tonalite in cement pore water has been tested with low ($1 \cdot 10^{-10}$ M to $1 \cdot 10^{-8}$ M) Nb concentrations (Kämäräinen et al. 1987, Kulmala & Hakanen 1993). In Kulmala & Hakanen (1993), the R_d values tend to increase with pH. At pH 12.7 in the cement modified groundwater, the R_d values were 2-4 m^3/kg. No solubility limitation of Nb concentration was expected in the sorption experiments, because the Ca-concentration in these waters was 20 mM, much lower than in the OLSR reference water, and the maximum Nb concentration was $7 \cdot 10^{-10}$ M.

15.2.1 Source data

Sorption on the reference rocks at pH 7-10 was determined by the batch method using radioactive tracer (Methodology described in Appendix 4). The experiments were performed in anoxic glacial meltwater OLGA, fresh ALLMR, brackish OLBA and saline OLSR reference waters. The R_d values are shown in Figures Nb-4 – Nb-7.

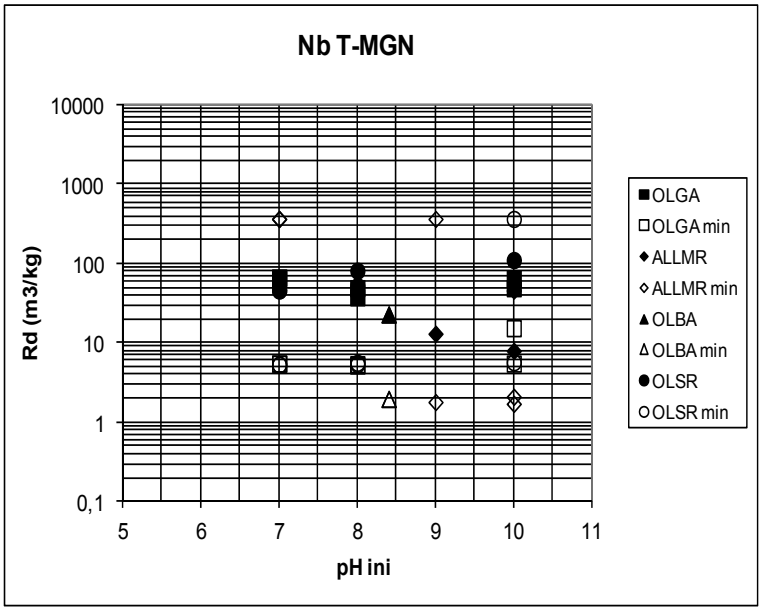

Figure Nb-4. *R_d values (m^3/kg) of niobium for Olkiluoto T-series mica gneiss T-MGN in anoxic conditions. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

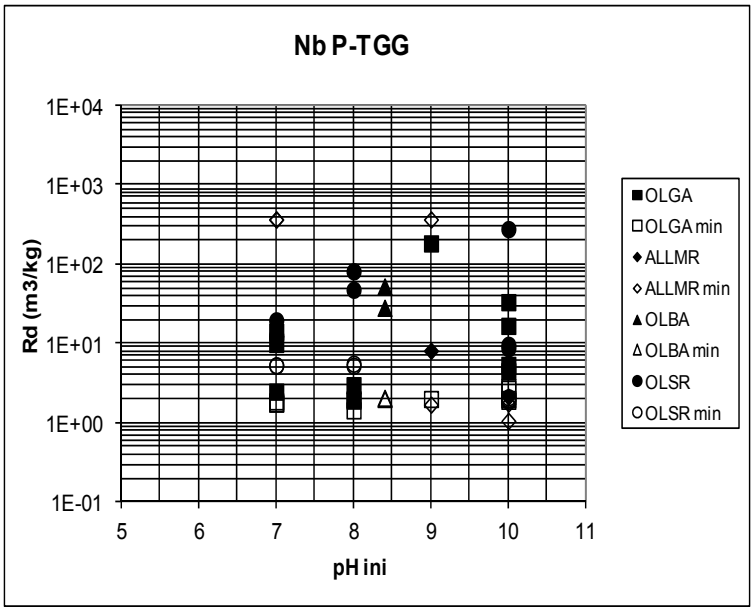

Figure Nb-5. *R_d values (m^3/kg) of niobium for Olkiluoto P-series tonalite granodiorite granite gneiss P-TGG in anoxic conditions. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

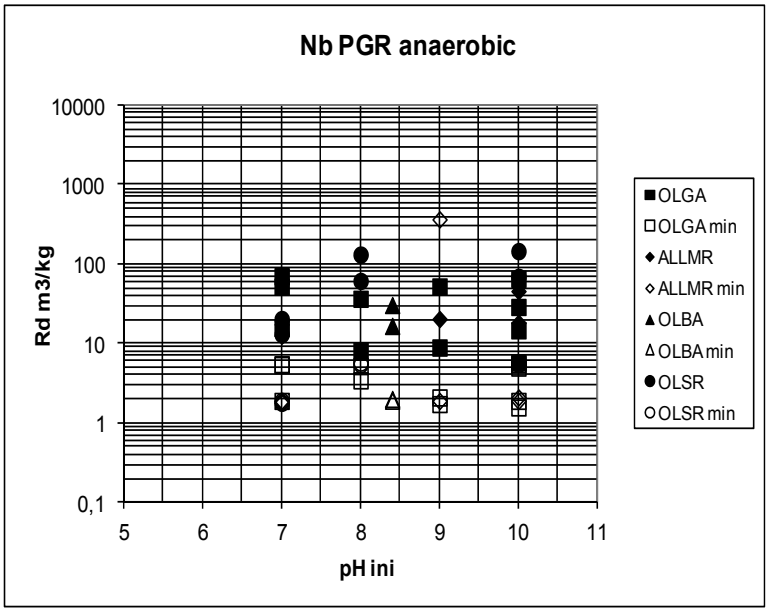

Figure Nb-6. *R_d values (m^3/kg) of niobium for Olkiluoto T-series tonalite granodiorite granite gneiss T-TGG in anoxic conditions. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

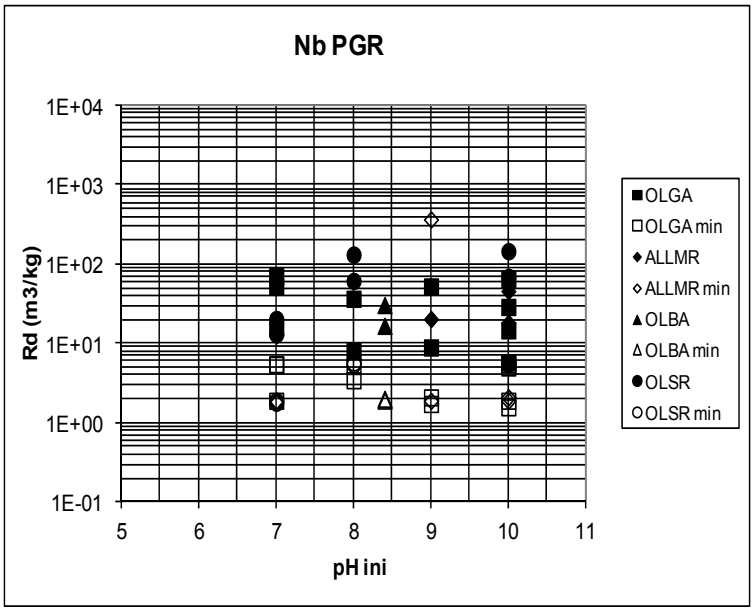

Figure Nb-7. *R_d, (m^3/kg) of niobium for Olkiluoto pegmatitic granite PRG in anoxic conditions. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

15.2.2 Best estimate K_d values

Owing to the high sorption of Nb, there was a large scatter in the measured R_d values (Figures Nb-4 – Nb-7). This brings uncertainty to the calculation of the best estimate K_d values. This was taken into account by choosing the lowest R_d values for each rock type and reference water for the calculation of the K_d values. Choosing the lowest value for a rock type led to an apparent dependency of Nb sorption on the water type. However, this disappeared when the uncertainty of the R_d values was considered. In the experiments, the separation between liquid and solid material was performed by centrifugation following filtration. Some sorption may occur on the filter, leading to high R_d values. Therefore, the lowest R_d value was chosen to represent all waters for the whole pH region. The best estimate K_d values were calculated from the R_d values using the conversion factors for the rocks.

The sorption experiments were performed only in anoxic glacial meltwater OLGA, fresh ALLMR, brackish OLBA and saline OLSR reference waters. Speciation of Nb in the waters indicated nothing but hydroxo complexes. Niobium is not redox sensitive and OLGA was chosen to represent the oxic OLGO, ALLMR to ALLMO and OLSR to OLSO reference water conditions. The brackish KR4_81_1 and saline KR20_465_1 groundwaters are similar to fresh ALLMR and saline OLSR reference waters, respectively, but contain more carbonate than the corresponding reference water. Since niobium speciation is not sensitive to carbonate concentration in the groundwaters, the best estimate K_d values in ALLMR are proposed for KR4_81_1 and those in OLSR for the KR20_465_1 waters. The best estimate K_d values for the rocks are given in Tables Nb-1 – Nb-4.

Table Nb-1. *Best estimate K_d values (m^3/kg) of niobium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.9E+00**	**1.9E+00**	**1.9E+00**	**1.9E+00**	**1.9E+00**	**1.9E+00**	**1.9E+00**	**1.9E+00**	**1.9E+00**
10	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00

NOTE: Large difference between K_d for T-MGN and P-TGG. Complementary evaluation using lower limit KGa-1b R_d value (45 m^3/kg) yields a lower limit K_d value of 1.4 m^3/kg for T-MGN and P-TGG.

Table Nb-2. *Best estimate K_d values (m^3/kg) of niobium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.9E-01**	**2.9E-01**	**2.9E-01**	**2.9E-01**	**2.9E-01**	**2.9E-01**	**2.9E-01**	**2.9E-01**	**2.9E-01**
10	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01

NOTE: Large difference between K_d for T-MGN and P-TGG. Complementary evaluation using lower limit KGa-1b R_d value (45 m^3/kg) yields a lower limit K_d value 1.4 m^3/kg for T-MGN and P-TGG.

Table Nb-3. *Best estimate K_d values (m^3/kg) of niobium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.2E-01**	**3.2E-01**	**3.2E-01**	**3.2E-01**	**3.2E-01**	**3.2E-01**	**3.2E-01**	**3.2E-01**	**3.2E-01**
10	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01

Table Nb-4. *Best estimate K_d values (m^3/kg) of niobium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.4E-01**	**2.4E-01**	**2.4E-01**	**2.4E-01**	**2.4E-01**	**2.4E-01**	**2.4E-01**	**2.4E-01**	**2.4E-01**
10	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01

15.2.3 Lower limit K_d values

The lower limit K_d values were calculated for the rocks by dividing the best estimate values by the uncertainty factor for each rock. These factors are shown in Table Nb-5. The scatter in R_d values is taken into account by choosing the lowest value. The lower limit K_d values are shown in Tables Nb-6 – Nb-9.

Table Nb-5. *The uncertainty factors of niobium for rocks. T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

Reference rock	Factor for random error calculation
T-MGN, P-TGG	4.5
T-TGG	20*
PGR	50*
*error propagation using the errors in the mica contents and BET/N_2 (surface area) of micas and crushed rock yield unrealistically low correction factor for T-MGN and PGR. Omitting the error in BET/N_2 of crushed rock, the factor for T-TGG is 7 and for PGR 43.	

Table Nb-6. *Lower limit K_d values (m^3/kg) of niobium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.2E-01**	**4.2E-01**	**4.2E-01**	**4.2E-01**	**4.2E-01**	**4.2E-01**	**4.2E-01**	**4.2E-01**	**4.2E-01**
10	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01

Table Nb-7. *Lower limit K_d values (m^3/kg) of niobium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**5.8E-02**	**5.8E-02**	**5.8E-02**	**5.8E-02**	**5.8E-02**	**5.8E-02**	**5.8E-02**	**5.8E-02**	**5.8E-02**
10	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02

Table Nb-8. *Lower limit K_d values (m^3/kg) of niobium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.6E-02**	**1.6E-02**	**1.6E-02**	**1.6E-02**	**1.6E-02**	**1.6E-02**	**1.6E-02**	**1.6E-02**	**1.6E-02**
10	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02

Table Nb-9. *Lower limit K_d values (m^3/kg) of niobium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.2E-02**	**1.2E-02**	**1.2E-02**	**1.2E-02**	**1.2E-02**	**1.2E-02**	**1.2E-02**	**1.2E-02**	**1.2E-02**
10	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02

15.3 Sorption on clays

Sorption of Nb on rocks in Kulmala & Hakanen (1993) was higher at high pH in cement modified groundwater than at pH typical of natural groundwaters. Speciation of Nb indicates (Figures Nb-1, Nb-2) that at high pH the dominant species are anionic, which suggests that the K_d values decrease rapidly with the increase at pH higher than 8. This was verified by sorption experiments for kaolinite, illite and chlorite in the reference waters and in Na-perchlorate and Ca-perchlorate solutions using radioactive tracer (Methodology described in Appendix 4).

Sorption on kaolinite KGa-1b and illite IMt-1 in $NaClO_4$ and $Ca(ClO_4)_2$ solutions indicate that the cation composition of the solution had an effect on the sorption of Nb (Figures Nb-5 – Nb-6). In the experiments, the Nb concentration was much lower than the solubility of Nb_2O_5 or $Ca(NbO_3)_2$. The difference in sorption in $NaClO_4$ and $Ca(ClO_4)_2$ solutions is obvious. In Ca-perchlorate experiments, R_d was practically not decreased with an increase of pH, as in Na-perchlorate solution, where a decrease of R_d (100 m^3/kg to 10 m^3/kg) with increasing pH was observed.

15.3.1 Source data

In all reference waters, high sorption of Nb was found. The R_d values were almost the same for the whole pH range studied. The best estimate values are calculated from the R_d values of the experiments shown in Figures Nb-10 – Nb-12.

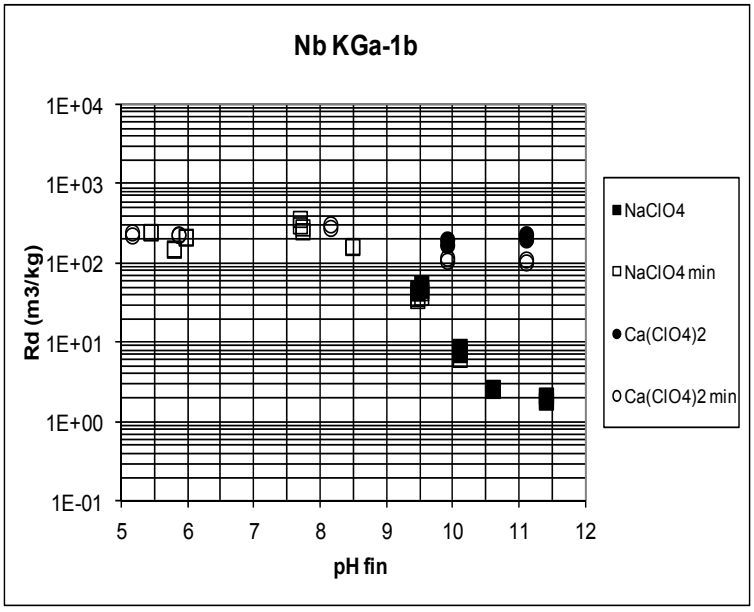

Figure Nb-8. *R_d values (m^3/kg) of niobium for kaolinite in anoxic Na- and Ca-perchlorate solutions. pH is the pH after completing the experiment. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

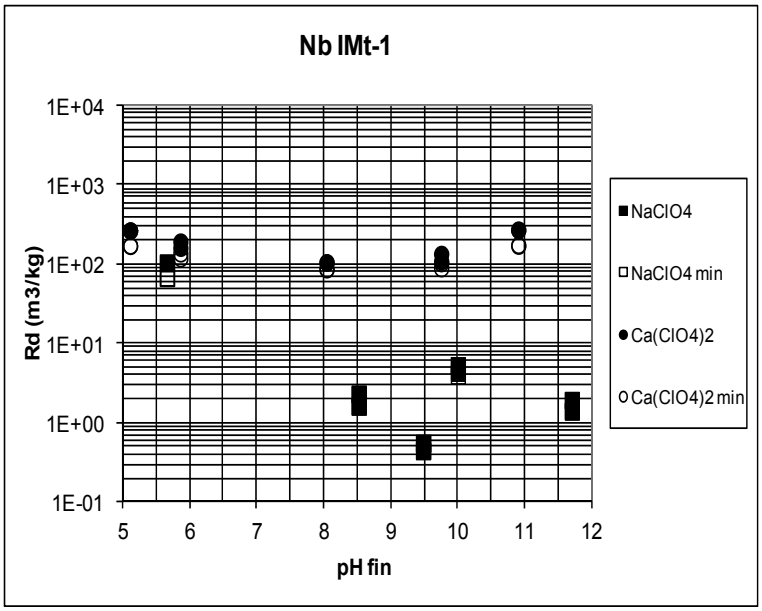

Figure Nb-9. *R_d values (m^3/kg) of niobium for illite in anoxic Na- and Ca-perchlorate solutions. pH is the initial pH at the experiment. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

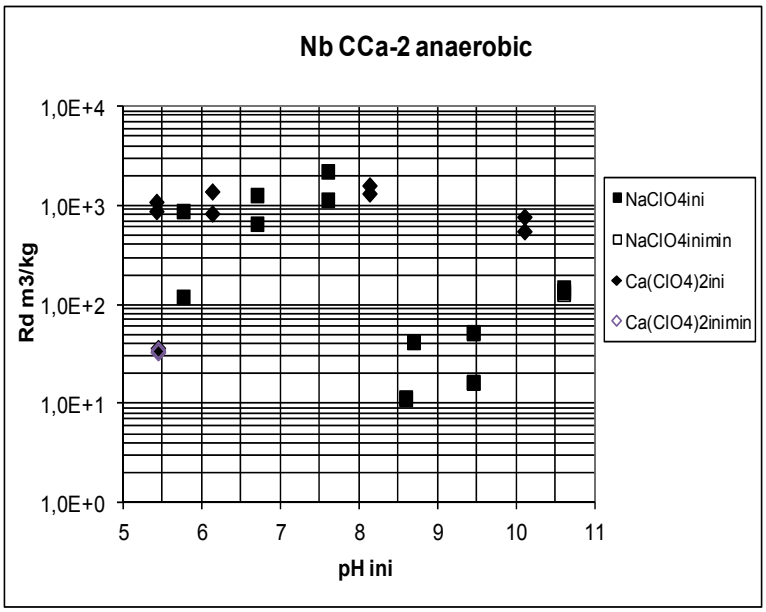

Figure Nb-10. *R_d values (m^3/kg) of niobium for chlorite (ripidolite) in anoxic Na- and Ca-perchlorate solutions. pH is the initial pH at the experiment. The minimum (min) values are based on 1σ counting error of the radioactive tracer. For some samples only the minimum value could be determined.*

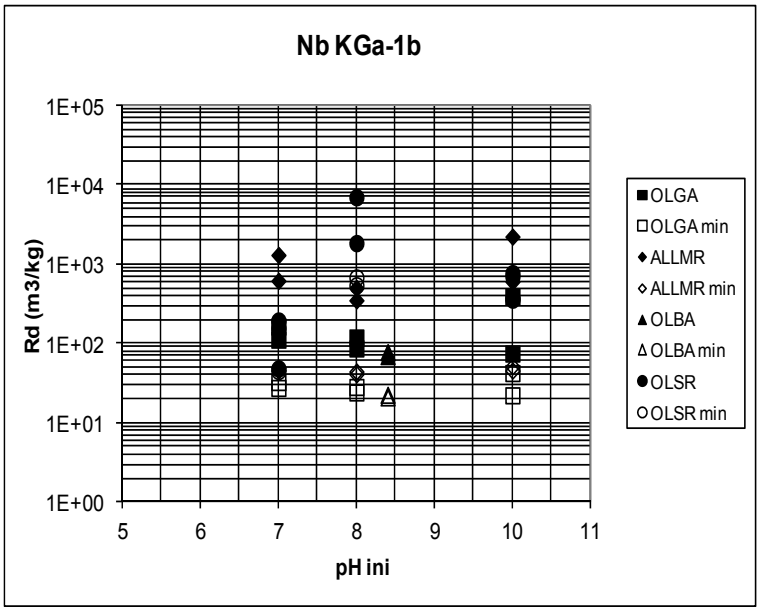

Figure Nb-11. *R_d values (m^3/kg) of niobium for kaolinite in anoxic OLGA, ALLMR, OLBA and OLSR reference waters. pH is the initial pH at the experiment. The minimum (min) values are based on 1σ counting error of the radioactive tracer.*

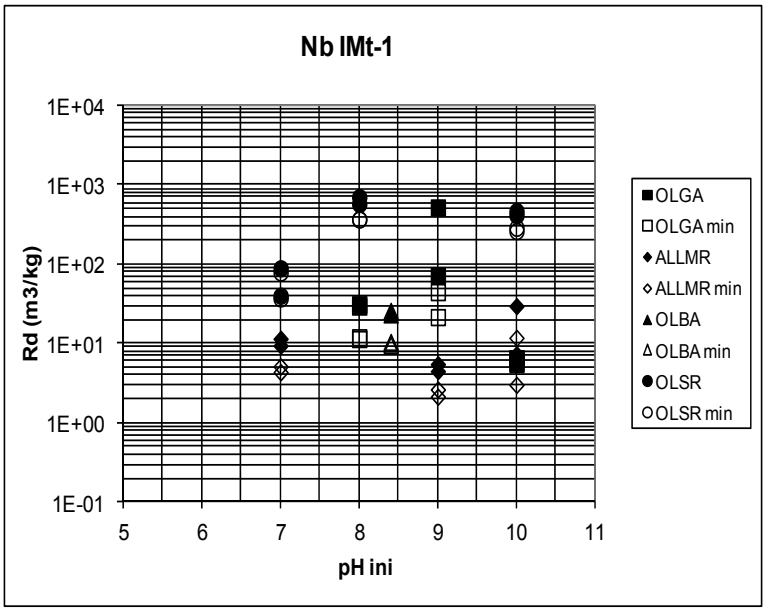

Figure Nb-12. *R_d values (m^3/kg) of niobium for illite in anoxic OLGA, ALLMR, OLBA and OLSR reference waters. pH is the initial pH at the experiment. The minimum (min) values are based on 1σ counting error of the radioactive tracer.*

15.3.2 Best estimate K_d values

Owing to the high sorption of Nb, there was a large scatter in the measured R_d values. The uncertainty in R_d values was taken into account by choosing the lowest R_d values for each clay and reference water for the calculation of the K_d values. No significant difference in sorption was observed when the error in R_d values was considered. Therefore, the lowest R_d value was chosen for all waters for the whole pH region. The experiments were performed only in anoxic OLGA, ALLMR, OLBA and OLSR reference waters. Since no difference in speciation is expected between the waters, the same K_d values can be used for all waters. The best estimate K_d values for clays are shown in Tables Nb-10 – Nb-12.

For chlorite (ripidolite) CCa-2, the sorption experiments were performed only in Na- and Ca-perchlorate solutions. The lowest R_d value in Ca-perchlorate solution was conservatively proposed as the K_d value in the reference waters (Figure Nb-10). This value is lower than that for illite and kaolinite in the reference waters.

The brackish KR4_81_1 and saline KR20_465_1 groundwaters are similar to ALLMR and OLSR reference waters, respectively, but contain more carbonate than the corresponding reference waters. Since niobium speciation is not sensitive to carbonate concentration in the groundwaters, the same best estimate K_d values for clays as in the other waters is proposed.

Table Nb-10. *Best estimate K_d values (m^3/kg) of niobium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

	Kaolinite								
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.9E+01**	**4.9E+01**	**4.9E+01**	**4.9E+01**	**4.9E+01**	**4.9E+01**	**4.9E+01**	**4.9E+01**	**4.9E+01**
10	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01

Table Nb-11. *Best estimate K_d values (m^3/kg) of niobium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

	Illite								
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.5E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**
10	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00

Table Nb-12. *Best estimate K_d values (m^3/kg) of niobium for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

	Chlorite								
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.4E+01**	**3.4E+01**	**3.4E+01**	**3.4E+01**	**3.4E+01**	**3.4E+01**	**3.4E+01**	**3.4E+01**	**3.4E+01**
10	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01

15.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays at Olkiluoto is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source}*UF_{model}*UF_{CEC}*UF_{spec}*UF_{pH}*UF_{lab\_field} \quad \text{(Nb-1)}$$

The lower limit of the K_d(LL) is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\ (LL) = K_d(BE)/UF_{tot} \quad \text{(Nb-2)}$$

Kaolinite

UF_{source} = 1.1. Owing to the high sorption of Nb, there was a large scatter in the measured R_d values. This brings uncertainty, which was taken into account by choosing the lowest R_d values for the calculations of K_d values.

UF_{model} = 1. No model was used.

UF_{CEC} = 1. The sorption mechanism is assumed to be surface complexation. Since the source data were performed in well-crystallised kaolinite KGa-1b, there is no need for a correction factor concerning differences between the source data and reference conditions. Well-crystallised kaolinite sorbs in equal amounts or less compared with the Olkiluoto kaolinite (the state of crystallinity was unknown). The CEC for kaolinite is in general not very high and it was considered that the uncertainty is not significant.

UF_{spec} varies from 1 to 1.4. When the experiment was performed in the reference water and its pH, the uncertainty factor UF_{spec} is taken to be 1, otherwise it is taken to be 1.4.

UF_{pH} = 1. No pH dependency of R_d values was observed and the source data are used without pH calculation.

UF_{lab_field} = 2. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 2.2 to 3.1.

The uncertainty factors are collected in Table Nb-13. Only those factors which are greater than one are listed. Also, if the correction factors are the same for reference pH and pH 10, only one is reported.

The lower limit K_d values for kaolinite, at Olkiluoto are given in Table Nb-15.

Illite

UF_{source} = 2.1. The source R_d data used for the calculation of K_d values for illite was more scattered than the data for kaolinite. This is taken into account by using a larger UF_{source} value than for kaolinite.

Table Nb-13. *The uncertainty factors (UF) of Nb for kaolinite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{spec}	$UF_{Lab\ field}$	UF_{tot}
OLGA	5.8	1.1	1.4	2	3.1
	10	1.1	1	2	2.2
OLGO	-	1.1	1.4	2	3.1
ALLMR	8.8	1.1	1	2	2.2
ALLMO	-	1.1	1.4	2	3.1
OLBA	7.6	1.1	1	2	2.2
	10	1.1	1.4	2	3.1
OLSR	8.3	1.1	1	2	2.2
OLSO	-	1.1	1.4	2	3.1
KR4	-	1.1	1.4	2	3.1
KR20	-	1.1	1.4	2	3.1

UF_{CEC} = 1.3. The possible difference in CEC values between IMt-1 illite and Olkiluoto illite is taken into account in the uncertainty factor UF_{CEC}. This uncertainty factor covers differences in CEC of most illites for which there are data in the literature.

The other UF factor values are the same as for kaolinite.

UF_{tot} varies from 5.5 to 7.6.

The uncertainty factors are collected in Table Nb-14. Only those factors which are greater than one are listed. Also, if the correction factors are the same for reference pH and pH 10, only one is reported.

The lower limit K_d values for kaolinite at Olkiluoto are given in Table Nb-16.

Chlorite

For chlorite at Olkiluoto, the uncertainty factors are the same as for illite (Table Nb-14).

The lower limit K_d values for kaolinite at Olkiluoto are given in Table Nb-17.

Table Nb-14. *The uncertainty factors (UF) of Nb for illite and chlorite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{CEC}	UF_{spec}	$UF_{Lab\ field}$	UF_{tot}
OLGA	5.8	2.1	1.3	1.4	2	7.6
	10	2.1	1.3	1	2	5.5
OLGO	-	2.1	1.3	1.4	2	7.6
ALLMR	-	2.1	1.3	1	2	5.5
ALLMO	-	2.1	1.3	1.4	2	7.6
OLBA	7.6	2.1	1.3	1	2	5.5
	10	2.1	1.3	1.4	2	7.6
OLSR	-	2.1	1.3	1	2	5.5
OLSO	-	2.1	1.3	1.4	2	7.6
KR4	-	2.1	1.3	1.4	2	7.6
KR20	-	2.1	1.3	1.4	2	7.6

Table Nb-15. *Lower limit K_d (m^3/kg) values of Nb for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.6E+01**	**1.6E+01**	**2.2E+01**	**1.6E+01**	**2.2E+01**	**2.2E+01**	**1.6E+01**	**1.6E+01**	**1.6E+01**
10	2.2E+01	1.6E+01	2.2E+01	1.6E+01	1.6E+01	2.2E+01	1.6E+01	1.6E+01	1.6E+01

Table Nb-16. *Lower limit K_d (m^3/kg) values of Nb for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**5.9E-01**	**5.9E-01**	**8.2E-01**	**5.9E-01**	**8.2E-01**	**8.2E-01**	**5.9E-01**	**5.9E-01**	**5.9E-01**
10	8.2E-01	5.9E-01	8.2E-01	5.9E-01	5.9E-01	8.2E-01	5.9E-01	5.9E-01	5.9E-01

Table Nb-17. *Lower limit K_d (m^3/kg) values of Nb for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

	Chlorite								
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**4.5E+00**	**4.5E+00**	**6.2E+00**	**4.5E+00**	**6.2E+00**	**6.2E+00**	**4.5E+00**	**4.5E+00**	**4.5E+00**
10	6.2E+00	4.5E+00	6.2E+00	4.5E+00	4.5E+00	6.2E+00	4.5E+00	4.5E+00	4.5E+00

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16 ZIRCONIUM

16.1 Speciation

Zirconium is not redox sensitive in the geosphere and is at the Zr(IV) oxidation state. The chemistry of Zr in natural waters is dominated by Zr-hydroxo complexes. Only at pH 4 and lower, the fluoride complexes are formed in small proportions in the saline OLSR reference water (Figure Zr-1). In all reference waters, more than 99 % of Zr is in the form of the $Zr(OH)_4$ complex. The solubility of Zr in the waters is $1.6 \cdot 10^{-8}$ M (Grivé et al. 2008), when estimated to be controlled by the amorphous tetrahydroxide $Zr(OH)_4(am)$.

Sasaki et al. (2006, 2008) measured and modelled the solubility of Zr-hydroxide system in carbonate-free solution. Their results suggest that the solubility of $ZrO_2(OH)_4$ is $1 \cdot 10^{-14}$ to $9 \cdot 10^{-9}$ M. Formation of several soluble zirconium carbonato- and hydroxocarbonato complexes were studied by Veyland et al. (2000). A high increase of zirconia solubility was measured by Pouchon et al. (2001) at carbonate concentrations higher than 10 mM. The solubility increased from 10^{-10} M - 10^{-8} M in carbonate-free water to 10^{-6} M - 10^{-5} M in 50 mM $NaHCO_3$ solution. In the reference waters, the carbonate concentrations are too low to increase the solubility of Zr. The proportion of Zr carbonato complexes in the high-carbonate brackish reference water OLBA is less than 0.5 %.

Owing to the fact that the dominant oxidation state is Zr(IV) and their high tendency to hydrolyse, Zr and Th are often taken to be chemical analogues.

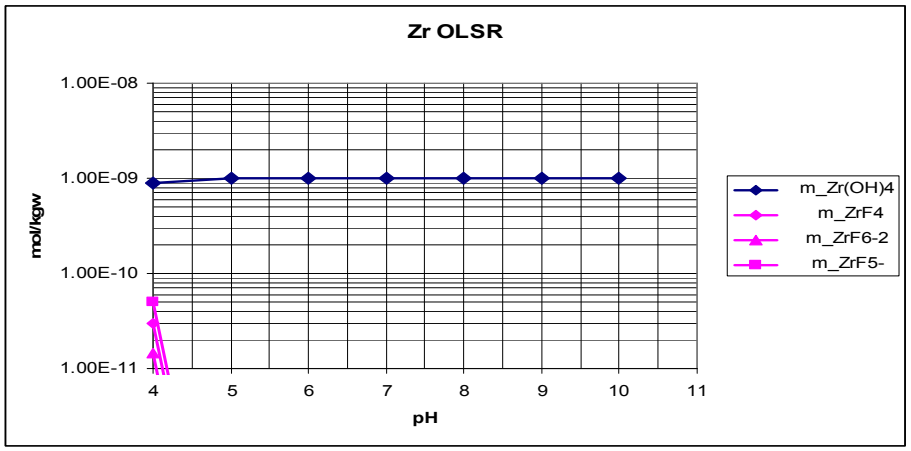

***Figure Zr-1**. Speciation of zirconium in saline reference water OLSR.*

16.2 Sorption on rocks

16.2.1 Source data

Sorption of Zr was determined in in-house experiments by Kulmala & Hakanen (1993) and by Kämäräinen et al. (1987) on the Olkiluoto tonalite in brackish PVA-2 groundwater and Allard (ALL) water respectively. The values found by Kämäräinen et

al. (1987) are higher than those in Kulmala & Hakanen (1993). There is a large difference in R_d values between centrifuged and additionally filtered samples by Kämäräinen et al. (1987). In some of the experiments of Kulmala & Hakanen (1993), the initial Zr concentration was higher than the solubility of Zr, and formation colloidal Zr solid cannot be ruled out. Due to uncertainties in the in-house R_d values for Zr, the K_d values of Zr are estimated using a chemical analogue.

16.2.2 Best estimate K_d values

Zr(IV) shows the same type of hydroxo, carbonato and hydroxocarbonato complexation behaviour as Th(IV). The hydrolysis constants of Zr are larger than those of Th and even larger than those of Pu(IV) and Np(IV). The LFER (Linear Free Energy Relationship) suggests that the sorption of Zr in the groundwaters is at least as high as that of Th (Dzombak & Morel 1990, Bradbury & Baeyens 2005). It is suggested that for Zr in all reference waters, the same best estimate K_d values as Th are used (see Chapter 20.2.2). The best estimate K_d values for rocks are listed in Tables Zr-1 – Zr-4.

Table Zr-1. *Best estimate K_d values (m^3/kg) of zirconium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**
10	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00

Table Zr-2. *Best estimate K_d values (m^3/kg) of zirconium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Zr-3. *Best estimate K_d values (m^3/kg) of zirconium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Zr-4. *Best estimate K_d values (m^3/kg) of zirconium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-01**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**
10	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00

16.2.3 Lower limit K_d values

Zr is proposed in all waters to have the same best estimate K_d values as Th. Also, the lower limit K_d values for Zr are the same as for Th (see Chapter 20.2.3). The lower limit K_d values for rocks are listed in Tables Zr-5 – Zr-8.

Table Zr-5. *Lower limit K_d values (m^3/kg) of zirconium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**
10	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01

Table Zr-6. *Lower limit K_d values (m^3/kg) of zirconium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-02**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Zr-7. *Lower limit K_d values (m^3/kg) of zirconium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E-02**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Zr-8. *Lower limit K_d values (m^3/kg) of zirconium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**
10	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02

16.3 Sorption on clays

16.3.1 Source data

Since no in-house or open-source data are available on Zr sorption on clays, Th(IV) is used as an analogue.

16.3.2 Best estimate K_d values

It was suggested that the sorption of Zr on rocks has the same best estimate K_d values as Th in all reference waters. The best estimate K_d values of Th for clays are also proposed for Zr (see Chapter 20.3.2). The best estimate K_d values for clays are listed in Tables Zr-9 – Zr-10.

16.3.3 Lower limit K_d values

The lower limit K_d values of Th are suggested as the lower limit K_d values for zirconium (see Chapter 20.3.3). The lower limit K_d values for clays are listed in Tables Zr-11 – Zr-12.

Table Zr-9. *Best estimate K_d values (m^3/kg) of zirconium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E+01**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**
10	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02

Table Zr-10. *Best estimate K_d values (m^3/kg) of zirconium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**
10	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01

Table Zr-11. *Lower limit K_d (m^3/kg) values of zirconium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E+01**	**8.4E+01**	**8.3E+01**	**8.4E+01**	**6.0E+01**	**6.0E+01**
10	8.4E+01	8.4E+01	8.4E+01	8.4E+01	6.0E+01	6.0E+01

Table Zr-12. *Lower limit K_d (m^3/kg) values of zirconium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E+00**	**7.5E+00**	**7.5E+00**	**7.5E+00**	**5.3E+00**	**5.3E+00**
10	7.5E+00	7.5E+00	7.5E+00	7.5E+00	5.3E+00	5.3E+00

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17 PALLADIUM

17.1 Speciation

The modelled speciation of Pd in Figure Pd-1 indicates that in glacial meltwater OLGA and fresh reference water ALLMR, the only Pd(II) species is the neutral $Pd(OH)_2$. In brackish reference water OLBA (Figure Pd-2), brackish groundwater KR4_81_1 (Figure Pd-3) and saline reference water OLSR (Figure Pd-4), the contribution of anionic chloride complexes in the low-pH region increases with chloride concentration. In the oxic saline reference water (OLSO) at pH 7.2, the chloride complexes reduce the proportion of $Pd(OH)_2$ to 70 %. Kitamura & Yui (2010) have re-evaluated the hydrolysis constants of palladium. At the pH range of interest in this report (pH 6-10), the major change is that the fraction of chloride complexes in the OLSO reference water at pH 7.2 is 12 %, lower than previously estimated (Figure Pd-5). The proportion of ammonia complexes in KR4_81_1 (Figure Pd-3) is less than 1 % at pH 7.8 and around 15 % at pH 10.

The redox conditions in all reference waters except OLGA under oxic conditions favour the reduction of Pd (II) to metallic Pd(0) state with extremely low solubility in the waters.

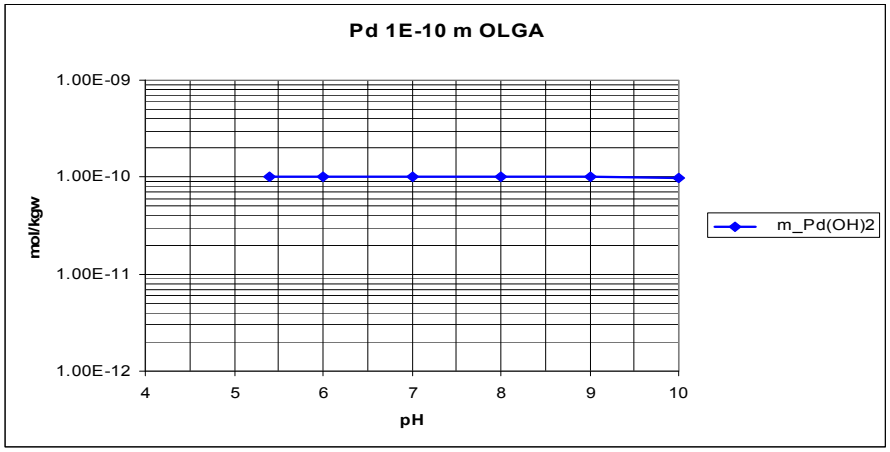

Figure Pd-1. *Speciation of Pd in the glacial meltwater OLGA.*

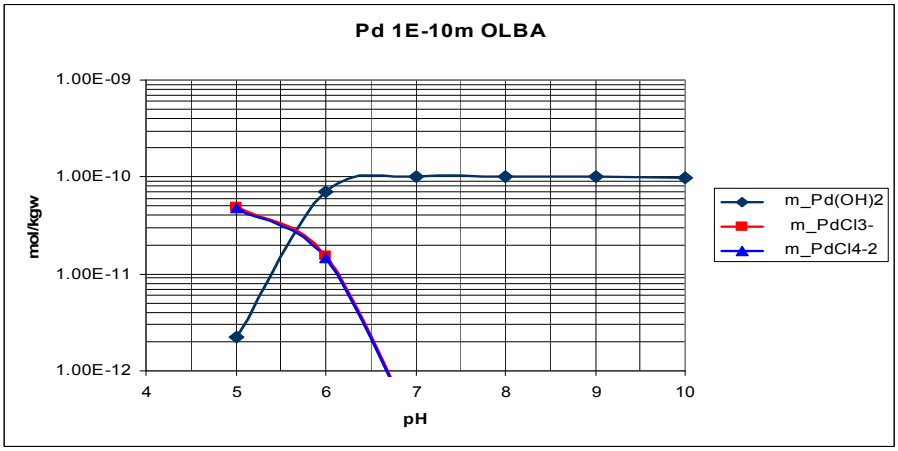

Figure Pd-2. *Speciation of Pd in the brackish reference water OLBA.*

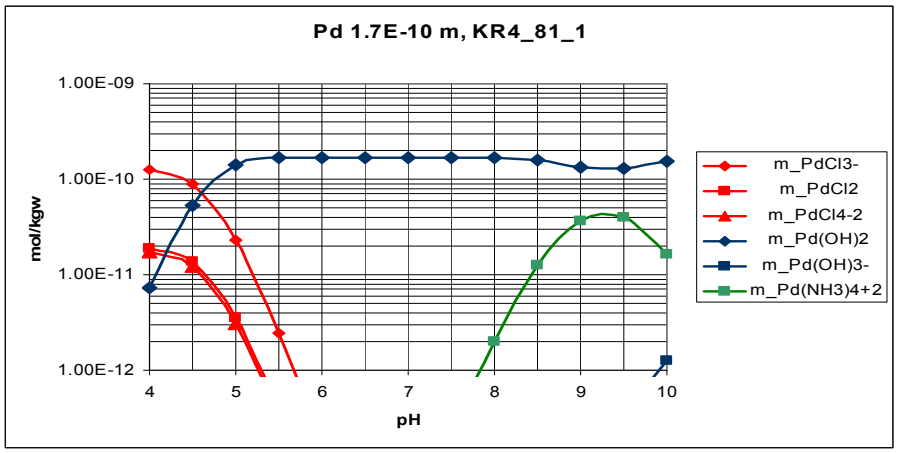

Figure Pd-3. *Speciation of Pd in the brackish groundwater KR4_81_1.*

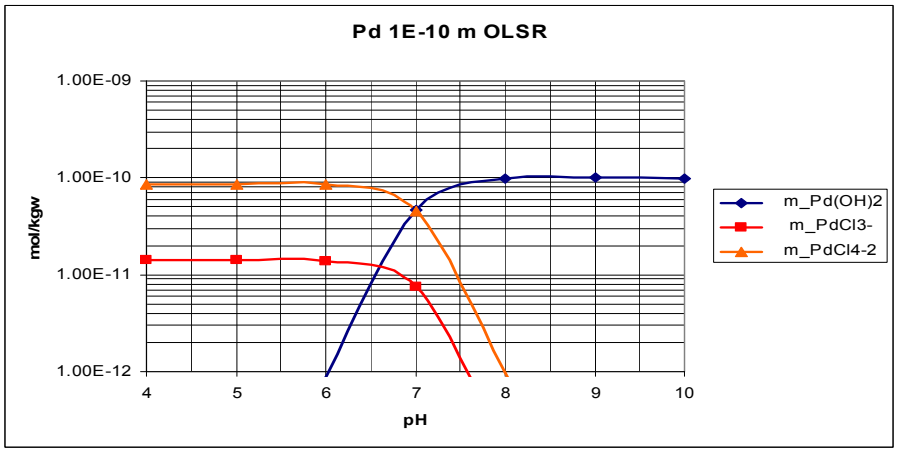

Figure Pd-4. *Speciation of Pd in saline reference water OLSR.*

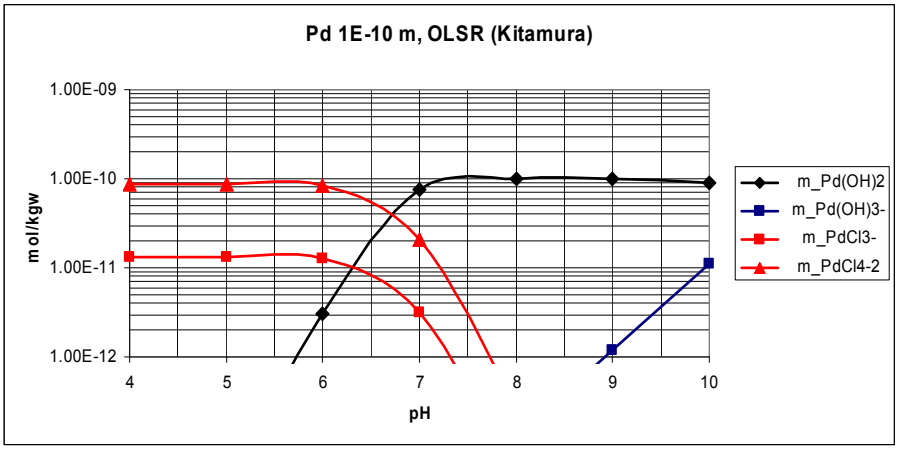

Figure Pd-5. *Speciation of Pd in saline reference water OLSR using the newly evaluated hydrolysis log k values in Kitamura & Yui (2010).*

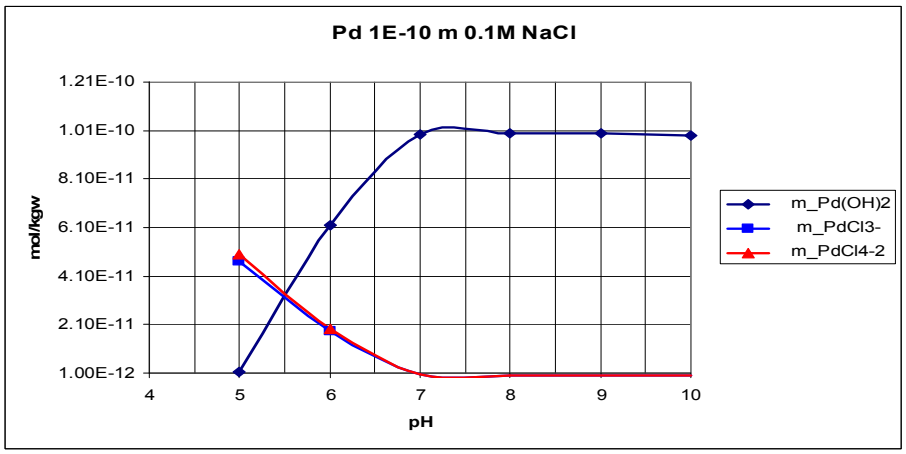

Figure Pd-6. *Speciation of Pd in the 0.1 M NaCl solution.*

17.2 Sorption on rocks

17.2.1 Source data

The sorption data of Pd in the Japanese sorption database JNC SDB (JAEA) include R_d values for granodiorite (from Tachi et al. (1999)). The values were determined in 0.01 to 0.1 M NaCl solutions with initial Pd concentration of $5 \cdot 10^{-8}$ M. The reported R_d values are higher at pH 5 than at pH 11 and higher for the higher solution to solid ratio. The latter indicates that probably some other mechanism than equilibrium sorption was responsible for the decrease of solution concentration. The speciation of Pd in 0.1 M NaCl solution in Figure Pd-6 does not support this kind of sorption behaviour.

Comparing the calculated speciation in 0.1 NaCl (Figure Pd-6) with pH edge (pH 4 – 6) of sorption on soils in 0.1 M KCl in Sako et al. (2009) indicates that the sorption increases with the increase of proportion of hydrolysed species $Pd(OH)_2$. The sorption on the soils was 100 %, but the R_d values increase with the increase of initial solution

concentration ($5 \cdot 10^{-7}$ M to $5 \cdot 10^{-5}$ M), making it questionable whether these values represent only sorption.

It follows that no reliable sorption values of Pd for rocks have come to the attention of the authors of this report. No in-house data for reference water conditions or for reference rocks are available.

17.2.2 Best estimate K_d values

Hydrolysis coefficients of Pd (II) have higher values than those of Ni (II), as indicated by the speciation of Ni and Pd in the waters. According to the LFER (Linear Free Energy Relationship) theory, the surface complexation constants of Pd are larger than those of Ni (Dzombak & Morel 1990, Bradbury & Baeyens 2005). Use of the K_d values of Ni for sorption of Pd thus most probably do not overestimate sorption of Pd (II). This is supported by the higher R_d values of Pd than of Ni for the kaolinite in a multitracer experiment on the removal of metals from seawater (Chen et al. 1996). The best estimate K_d values for Pd (II) are suggested to be the same as for Ni (II) (see Chapter 11.2.2). The best estimate K_d values for rocks are listed in Tables Pd-1 – Pd-4.

Table Pd-1. *Best estimate K_d values (m^3/kg) of palladium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-02**	**1.5E-02**	**2.9E+00**	**1.1E-01**	**6.0E-01**	**1.5E-01**	**7.0E-02**
10	5.9E+00	5.9E+00	5.9E+00	5.9E+00	5.9E+00	5.9E+00	5.9E+00

Table Pd-2. *Best estimate K_d values (m^3/kg) of palladium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-03**	**7.5E-03**	**1.5E+00**	**5.5E-02**	**3.0E-01**	**7.5E-02**	**3.5E-02**
10	3.0E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00	3.0E+00

Table Pd-3. *Best estimate K_d values (m^3/kg) of palladium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.5E-03**	**6.5E-03**	**1.3E+00**	**7.0E-02**	**2.6E-01**	**8.0E-02**	**2.9E-02**
10	2.6E+00	2.6E+00	2.6E+00	2.6E+00	2.6E+00	2.6E+00	2.6E+00

Table Pd-4. *Best estimate K_d values (m^3/kg) of palladium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.6E-03**	**2.6E-03**	**5.1E-01**	**2.0E-02**	**3.5E-01**	**3.0E-02**	**1.2E-02**
10	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00	1.1E+00

17.2.3 Lower limit K_d values

Based on the above mentioned reasoning, the lower limit K_d values for Pd (II) are suggested to be the same as for Ni (II). The uncertainty factors of the Olkiluoto rocks for Ni were used (see Chapter 11.2.3). The lower limit K_d values for rocks are listed in Tables Pd-5 – Pd-8.

Table Pd-5. *Lower limit K_d values (m^3/kg) of palladium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-04**	**7.5E-04**	**1.5E-01**	**5.5E-03**	**3.0E-02**	**7.5E-03**	**3.5E-03**
10	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01	3.0E-01

Table Pd-6. *Lower limit K_d values (m^3/kg) of palladium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.8E-04**	**3.8E-04**	**7.5E-02**	**2.8E-03**	**1.5E-02**	**3.8E-03**	**1.8E-03**
10	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01

Table Pd-7. *Lower limit K_d values (m^3/kg) of palladium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.3E-04**	**3.3E-04**	**6.5E-02**	**3.5E-03**	**1.3E-02**	**4.0E-03**	**1.5E-03**
10	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01	1.3E-01

Table Pd-8. *Lower limit K_d values (m^3/kg) of palladium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.2E-05**	**5.2E-05**	**1.0E-02**	**4.0E-04**	**7.0E-03**	**6.0E-04**	**2.4E-04**
10	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02	2.2E-02

17.3 Sorption on clays

17.3.1 Source data

Chen et al. (1996) performed multitracer studies on the sorption of Pd on sea sediments and clay minerals montmorillonite and kaolinite. The R_d value for kaolinite in artificial seawater (24 g NaCl/L) was 9.3 m^3/kg at pH 7.5. No information about the properties of kaolinite was given, but the R_d for Pd can be compared with the R_d for Ni, which was 2.9 m^3/kg in the same conditions. This suggests a higher sorption of Pd than of Ni in accordance with the LFER theory, and the assumption that the use of K_d values for Ni and Pd do not overestimate sorption of Pd. Since no in-house or open-source data are available on Pd sorption on clays, Ni(II) is used as an analogue.

17.3.2 Best estimate K_d values

As previously suggested, the sorption of Pd on rocks has the same best estimate K_d values as Ni in all waters, and therefore also the best estimate K_d values for the clay minerals kaolinite and illite at Olkiluoto are taken as Ni. The best estimate K_d values for Pd (II) are suggested to be the same as for Ni (II) (see Chapter 11.3.2). The best estimate K_d values for clays are listed in Tables Pd-9 – Pd-10.

17.3.3 Lower limit K_d values

The lower limit K_d values for Pd (II) for the clay minerals kaolinite and illite at Olkiluoto are suggested to be the same as for Ni (II) (see Chapter 11.3.3). The lower limit K_d values for clays are listed in Tables Pd-11 – Pd-12.

Table Pd-9. *Best estimate K_d values (m^3/kg) of palladium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+00**	**1.0E+00**	**5.9E+00**	**6.5E-01**	**5.4E+00**	**1.0E+00**	**3.3E-01**
10	1.5E+01	1.5E+01	1.4E+01	1.4E+01	1.4E+01	1.3E+01	1.4E+01

Table Pd-10. *Best estimate K_d values (m^3/kg) of palladium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E+00**	**7.0E+00**	**1.2E+01**	**9.0E+00**	**9.3E+00**	**8.1E+00**	**9.4E+00**
10	1.6E+01	1.6E+01	1.5E+01	9.9E+00	9.9E+00	8.8E+00	9.9E+00

Table Pd-11. *Lower limit K_d (m^3/kg) values of Pd for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**9.1E-02**	**9.1E-02**	**5.9E-01**	**6.5E-02**	**5.4E-01**	**1.0E-01**	**3.3E-02**
10	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.4E+00	1.3E+00	1.4E+00

Table Pd-12. *Lower limit K_d (m^3/kg) values of Pd for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.7E-01**	**4.7E-01**	**1.1E+00**	**6.0E-01**	**8.5E-01**	**5.4E-01**	**6.3E-01**
10	1.1E+00	1.1E+00	1.4E+00	6.6E-01	9.0E-01	5.9E-01	6.6E-01

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18 TIN (Sn)

18.1 Speciation

Tin is a redox sensitive element. The most important Sn-mineral is cassiterite $Sn(IV)O_2(cr)$. The measured groundwater concentrations in crystalline bedrock (pH 8) have been $1 \cdot 10^{-9}$ M to $1 \cdot 10^{-8}$ M (Newcomb & Rimstidt 2002). Sn concentration has been measured in only a few groundwaters in Olkiluoto. In the Olkiluoto KR11 groundwater and in the granitic groundwater of Hästholmen, the Sn concentration was $4 \cdot 10^{-8}$ M to $1.7 \cdot 10^{-7}$ M (pH 7.6 – 8.7) (Hellä et al. 2014). The Sn-concentration in Opalinus clay pore water (pH 6.3) was around $4.5 \cdot 10^{-8}$ M (Van Loon et al. 2000).

The solubility of Sn in saline OLSR was calculated with the PHREEQC programme using the Thermo_Chimie Version 7b database (ANDRA 2009). $SnO_2(am)$ and $CaSn(OH)_6(s)$ were assumed to be the solubility limiting phases in the groundwater. Figure Sn-1 presents the calculated solubility of Sn in OLSR type water up to pH 12. At pH 11 and higher, the solubility is controlled by $CaSn(OH)_6(s)$. In the glacial, fresh and brackish groundwaters, $CaSn(OH)_6(s)$ is not a solubility limiting phase, as shown in Figure Sn-2 on the solubility of Sn in brackish water OLBA. Up to pH 10 of the groundwaters, the total solubility of Sn is the same in all reference waters. Speciation of soluble Sn in saline OLSR water (Figure Sn-3) indicates the decrease of $Sn(OH)_4$ species with increasing pH. The proportion of the $Sn(OH)_4$ that is expected to be the sorptive species in the groundwaters is less than 1 % at pH 10.

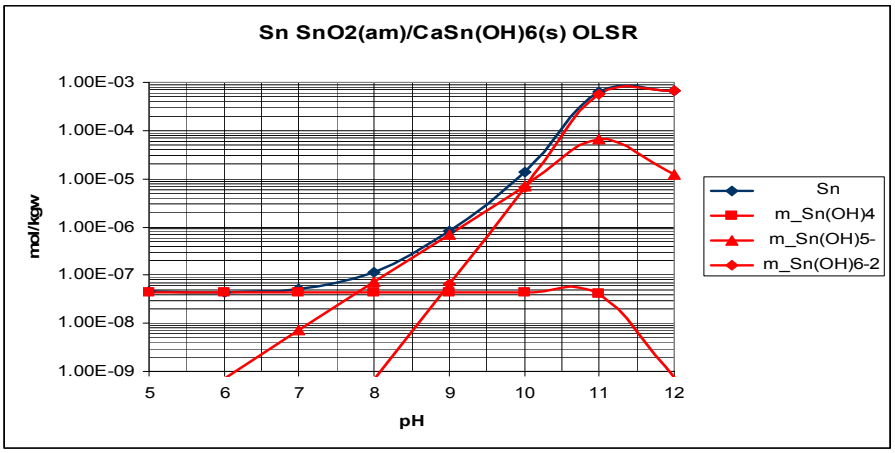

Figure Sn-1. *Solubility and speciation of tin (Sn) in saline OLSR water. Solubility limiting phases are $SnO_2(am)$ and $CaSn(OH)_6(s)$.*

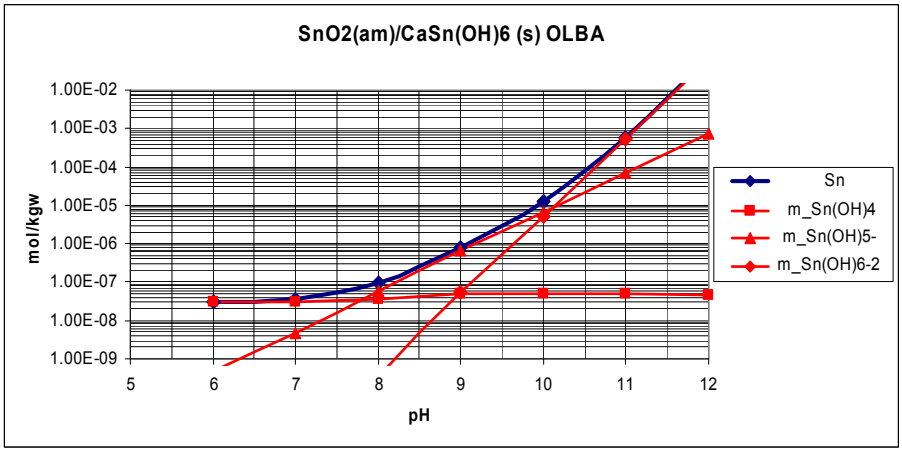

Figure Sn-2. *Solubility and speciation of tin (Sn) in brackish OLBA water. Solubility limiting phases in calculation were $Sn(OH)_4(am)$ and $CaSn(OH)_6(s)$*

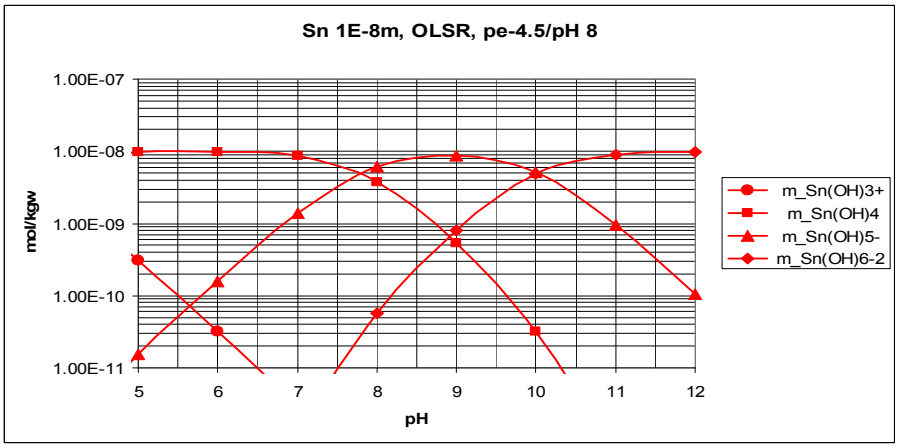

Figure Sn-3. *Speciation of tin (Sn) in saline OLSR water.*

18.2 Sorption on rocks

18.2.1 Source data

Sorption of Sn on the crushed reference rocks of Olkiluoto was determined using the batch method in fresh ALLMR and saline OLSR waters, using the Sn-113 isotope as a tracer. The rocks were T series mica gneiss (T-MGN), P series granodiorite gneiss (P-TGG), T series granodiorite gneiss (T-TGG) and pegmatite granite (PGR). The experimental method is described in Appendix 4. The R_d values are presented in Figures Sn-4 – Sn-7.

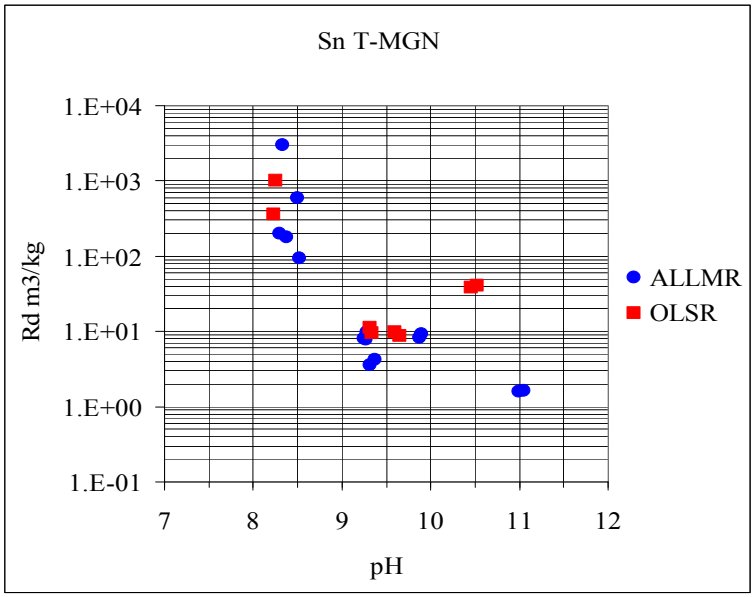

Figure Sn-4. *Calculated R_d values (m^3/kg) of Sn in fresh ALLMR and saline OLSR waters for T-MGN rock. Impact of possible partial precipitation of Sn at pH lower than 9 is included in these R_d values and was taken into account in calculation of R_d (see text).*

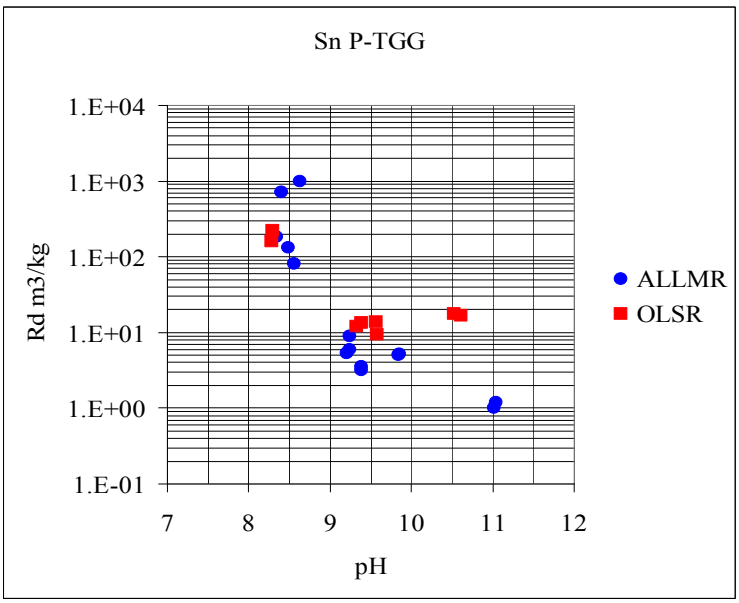

Figure Sn-5. *Calculated R_d values (m^3/kg) of Sn in fresh ALLMR and saline OLSR waters for P-TGG rock. Impact of possible partial precipitation of Sn at pH lower than 9 is included in these R_d values and was taken into account in calculation of R_d (see text).*

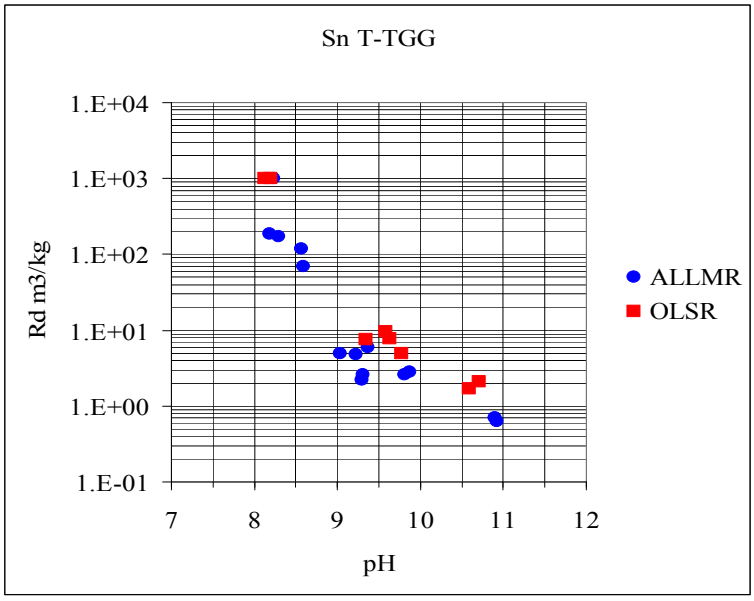

Figure Sn-6. *Calculated R_d values (m^3/kg) of Sn in fresh ALLMR and saline OLSR waters for T-TGG rock. Impact of partial precipitation of Sn at pH lower than 9 is included in these R_d values and was taken into account in derivation of R_d (see text).*

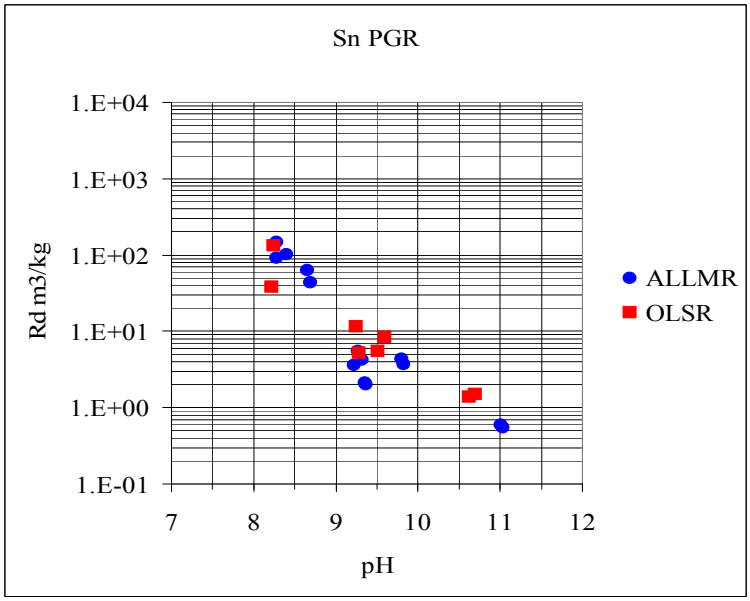

Figure Sn-7. *Calculated R_d values (m^3/kg) of Sn in fresh ALLMR and saline OLSR waters for PGR rock. Impact of partial precipitation of Sn at pH lower than 9 is included in these R_d values and was taken into account in derivation of R_d (see text).*

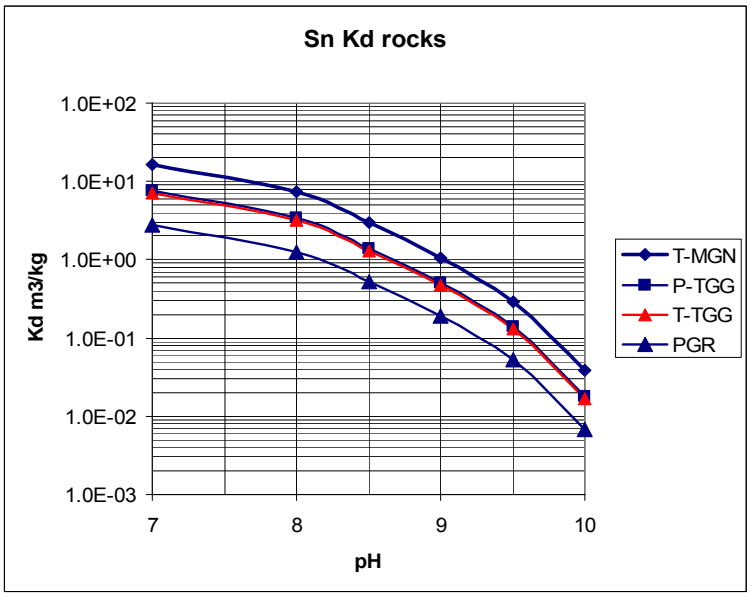

Figure Sn-8. *Calculated K_d values (m^3/kg) of Sn at pH range 7– 10 for Olkiluoto rocks. A first approach (see text).*

18.2.2 Best estimate K_d values

Owing to high carrier concentration in the tracer solution, the added total Sn concentration in the spiked solution, $6.7 \cdot 10^{-7}$ mol/L, was higher than the calculated solubility of $Sn(OH)_4(am)$ at pH 6–8. The final Sn concentrations in all experiments were, however, lower than the estimated solubility.

K_d values of Sn were calculated by two simplistic estimations, one by assuming that removal of Sn from the water was due to precipitation to the solubility limit of $Sn(OH)_4(am)$ followed by the sorption of soluble Sn to the rock, and one by starting at an R_d value at pH 9 when the initial Sn concentration was lower than the solubility at pH 9. In both estimations it was assumed that the anionic $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ complexes were non-sorbing.

In the first approach, an R_d value of 200 m^3/kg at pH 8 for T-MGN was used. The R_d value for the $Sn(OH)_4$ complex was calculated for T-MGN rock. Its proportion at pH 8 is 35%. After the subtraction of the impact of precipitated Sn from the R_d value, the rest was estimated to be due to sorption of the Sn that existed as $Sn(OH)_4$ at pH 8. For other pH values, the R_d values for T-MGN were calculated using the proportions of $Sn(OH)_4$ of Sn (Figure Sn-3) as the conversion factor. The R_d values for T-MGN were converted to K_d values using the conversion factor in Chapter 3 (Table 3-4). K_d values for the other reference rocks were converted from the value to T-MGN using the ratio of mica+hornblende contents of the rocks as the conversion factor to T-TGG and PGR. For P-TGG, only half of the mica+horblende concentration was used. The calculated K_d values of Sn for the rocks are presented in Figure Sn-8.

In the second approach, the K_d values for the rocks were calculated from the R_d value for T-MGN at pH 9 (10 m^3/kg), where the initial Sn concentration was lower than the calculated solubility. The R_d value for the $Sn(OH)_4$ species for T-MGN rock was calculated and converted to a lower pH by the proportion of $Sn(OH)_4$ of the total Sn. The calculated R_d values were converted to K_d values and are presented in Table Sn-1.

Table Sn-1. *Estimated K_d (m^3/kg) values of Sn for the reference waters in the pH range 7–10. The second approach (see text).*

pH	Rock			
	T-MGN	P-TGG	T-TGG	PGR
	m3/kg	m3/kg	m3/kg	m3/kg
7.0	2.8E+01	1.4E+01	1.3E+01	6.0E+00
7.5	2.0E+01	1.0E+01	9.0E+00	4.0E+00
8.0	1.2E+01	6.0E+00	6.0E+00	3.0E+00
8.5	6.0E+00	3.0E+00	3.0E+00	1.0E+00
9.0	2.0E+00	1.0E+00	9.0E-01	5.0E-01
9.5	5.0E-01	2.5E-01	2.0E-01	1.0E-01
10	1.0E-01	5.0E-02	5.0E-02	2.0E-02

The K_d values from the first approach (Figure Sn-8) are lower than the values from the second approach (Table Sn-1). Both estimations are very dependent on the thermo dynamic database. In the second approach the possible sorptivity of the anionic complexes affects the results more than in the first approach. The lower K_d values from the first approach are proposed as the best estimate values (Tables Sn-2 – Sn-5).

Sorption in OLGA (pH 5.8)

Speciation of Sn is the same for all reference waters. It is suggested that the best estimate K_d of Sn for the rocks at pH 5.8 (OLGA) is the same as that at pH 7 in the other waters. This is supported by the same R_d values (110 m^3/kg) at pH 7 and pH 6 being found in the experimental data for the Opalinus illite in Bradbury & Baeyens (2003).

Table Sn-2. *The best estimate K_d (m^3/kg) values of tin for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.6E+01**	**1.6E+01**	**1.8E+00**	**1.0E+01**	**4.0E+00**	**1.0E+01**	**1.0E+01**
10	3.6E-02	3.6E-02	3.6E-02	3.6E-02	3.6E-02	3.6E-02	3.6E-02

Table Sn-3. *The best estimate K_d (m^3/kg) values of tin for P series granodiorite gneiss P-TTG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.0E+00**	**8.0E+00**	**9.0E-01**	**5.0E-01**	**2.0E+00**	**5.0E+00**	**5.0E+00**
10	1.8E-02	1.8E-02	1.8E-02	1.8E-02	1.8E-02	1.8E-02	1.8E-02

Table Sn-4. *The best estimate K_d (m^3/kg) values of tin for T series granodiorite gneiss T-TTG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E+00**	**7.0E+00**	**7.0E-01**	**5.0E+00**	**1.9E+00**	**4.1E+00**	**5.0E+00**
10	1.7E-02	1.7E-02	1.7E-02	1.7E-02	1.7E-02	1.7E-02	1.7E-02

Table Sn-5. *The best estimate K_d (m^3/kg) values of tin for pegmatitic granite PGR in at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.8E+00**	**2.8E+00**	**3.0E-01**	**2.0E+00**	**7.0E-01**	**1.8E+00**	**2.1E+00**
10	7.0E-03	7.0E-03	7.0E-03	7.0E-03	7.0E-03	7.0E-03	7.0E-03

18.2.3 Lower limit K_d values

The uncertainty factor covers both the mineralogical and chemical uncertainties in solutions. The lower limit K_d value is calculated by dividing the best estimate value by the uncertainty factor.

The speciation shows that at pH 6 the $Sn(OH)_4$ is the main soluble species. For pH 6, there is no experimental sorption data to sorption on rocks. Sorption on Opalinus clay has been found to be the same at pH 6 to pH 8 (Lauber et al. 2000, Bradbury & Baeyens 2003). The removal of Sn from solution in experiments in this report is also the same. In the current experiments, the possible oversaturation of the solution with respect to $Sn(OH)_4$ (am) could not be excluded. The best estimate K_d values were derived using a solubility product value that gives low solubility of $Sn(OH)_4$: these values underestimate sorption of Sn. The uncertainty in K_d values is mostly due to the derivation of the K_d values from the R_d values for T-MGN for the other rock types. The factor due to mineralogical uncertainty is 5 for T-MGN and P-TGG. The chemical uncertainty owing to very low solubility of $Sn(OH)_4$(am) is difficult to quantify and it is regarded as sufficient to cover this by a factor of 4. The combined uncertainty factor for T-MGN and P-TGG is 20. For T-TGG and PGR the mineralogical uncertainty is estimated to be

high and it is taken here to be the dominating uncertainty, so no additional uncertainty is needed. The factors for rocks are presented in Table Sn-6. The lower limit K_d values of Sn for the Olkiluoto rocks in reference waters are presented in Tables Sn-7 – Sn-10.

Table Sn-6. *Uncertainty factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	20
T-TGG	20
P-TGG	20
PGR	50

Table Sn-7. *The lower limit K_d (m^3/kg) values of tin for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**8.0E-01**	**8.0E-01**	**9.0E-02**	**5.0E-01**	**2.0E-01**	**5.0E-01**	**5.0E-01**
10	1.8E-03	1.8E-03	1.8E-03	1.8E-03	1.8E-03	1.8E-03	1.8E-03

Table Sn-8. *The lower limit K_d (m^3/kg) values of tin for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**4.0E-01**	**4.0E-01**	**4.5E-02**	**2.5E-02**	**1.0E-01**	**2.5E-01**	**3.0E-01**
10	9.0E-04	9.0E-04	9.0E-04	9.0E-04	9.0E-04	9.0E-04	9.0E-04

Table Sn-9. *The lower limit K_d (m^3/kg) values of tin for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.5E-01**	**3.5E-01**	**3.5E-02**	**2.5E-01**	**9.5E-02**	**2.1E-01**	**3.0E-01**
10	8.5E-04	8.5E-04	8.5E-04	8.5E-04	8.5E-04	8.5E-04	8.5E-04

Table Sn-10. *The lower limit K_d (m^3/kg) values of tin for pegmatitic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.6E-02**	**5.6E-02**	**6.0E-03**	**4.0E-02**	**1.4E-02**	**3.6E-02**	**4.2E-02**
10	1.4E-04	1.4E-04	1.4E-04	1.4E-04	1.4E-04	1.4E-04	1.4E-04

18.3 Sorption on clays

18.3.1 Source data

The sorption of Sn on kaolinite KGa-1b was determined in fresh ALLMR, glacial OLGA and OLGO waters and on illite IMt-1 and on chlorite CCa-2 in ALLMR water. The experimental method is described in Appendix 4.

Kaolinite KGa-1b

The sorption of tin on kaolinite KGa-1b in fresh ALLMR, anaerobic glacial OLGA and aerobic glacial OLGO reference waters is presented in Figures Sn-9, Sn-10 and Sn-11.

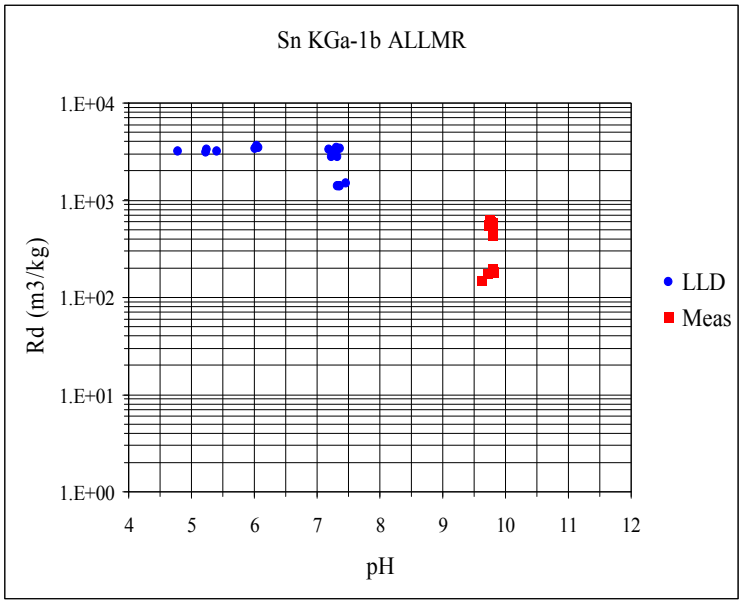

Figure Sn-9. *R_d values of Sn on kaolinite KGa-1b in fresh ALLMR reference water (LLD= limit of determination, Meas=measured value).*

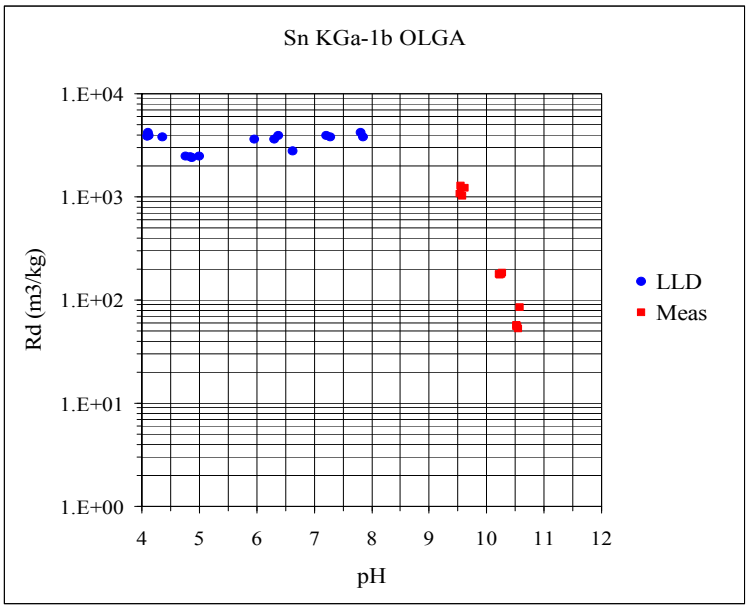

Figure Sn-10. *R_d values of Sn on kaolinite KGa-1b in anaerobic glacial OLGA reference water. (LLD= limit of determination, Meas = measured value).*

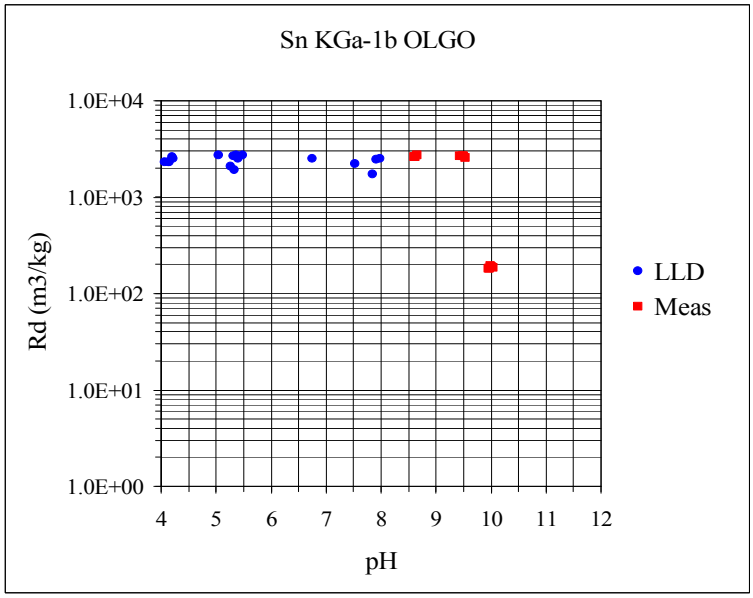

Figure Sn-11. *R_d values of Sn on kaolinite KGa-1b in aerobic glacial OLGO reference water. (LLD = limit of determination, Meas = measured value).*

Speciation calculations of Sn in the reference waters indicate that the $Sn(OH)_4$ species dominates at pH < 7 (Figure Sn-1). At higher pH, the anionic complexes $Sn(OH)_5^-$ and $Sn(OH)_6^{2-}$ are formed, and the solubility of Sn increases with pH. Sorption in the reference waters indicates constant R_d values at a pH lower than pH 7 and decrease of R_d with increase of pH at the high pH, in accordance with the speciation when the anionic species are assumed to be non-sorbing.

The initial Sn concentration in the experiments was $6.7 \cdot 10^{-7}$ M, higher than the calculated solubility of $4.7 \cdot 10^{-8}$ M. The high R_d values at pH < 8 may be affected by the solubility limitation of Sn. It follows that only the R_d values at pH 8 and higher are taken into account in the calculation of the K_d values of Sn for kaolinite in the reference waters.

The K_d values were estimated for $1 \cdot 10^3$ m^3/kg (OLGA pH 9.5) in all waters.

Illite IMt-1

The sorption of tin on IMt-1 illite was determined in fresh ALLMR water at pH 7–10.4. In the literature, the sorption was determined on Na-conditioned illite in 0.1 M $NaClO_4$ solution at pH 3–12 (Bradbury and Baeyens 2003).

The sorption mechanism is surface complexation and the dominating species are the same in 0.1 M $NaClO_4$ and in all reference waters. No dependence on ionic strength is expected. In both datasets, the decrease of sorption with increase of pH is less than the decrease in the proportion of $Sn(OH)_4$ and this suggests that the anionic hydroxo complexes $Sn(OH)_5^-$ and possibly $Sn(OH)_6^{2-}$ are also sorbing to some extent.

For pH 7–9, the lowest R_d value is 115 m^3/kg and most values are higher than 150 m^3/kg. The best estimate R_d value is proposed to be 150 m^3/kg for all waters.

The best estimate value at pH 10 is interpolated to be between 150 m^3/kg at pH 9.7 and 60 m^3/kg at pH 10.3. The values derived from experiments in the ALLMR water are proposed as the best estimate values for all waters.

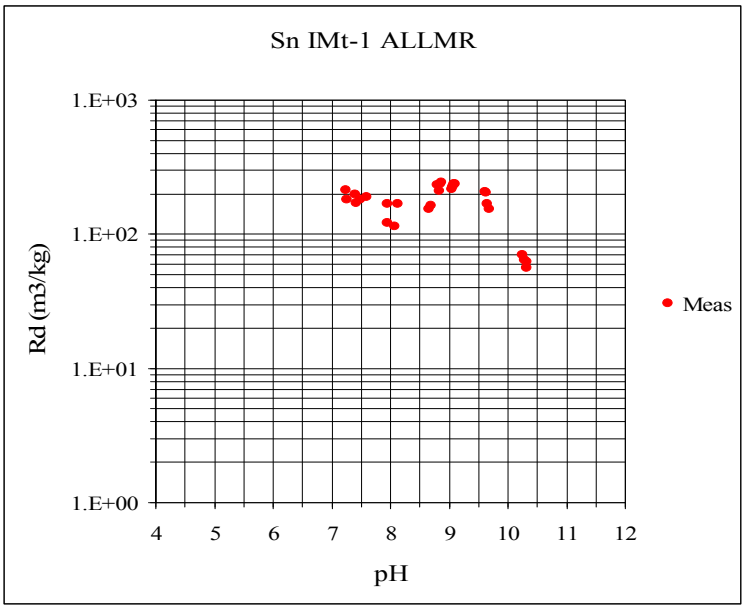

Figure Sn-12. *R_d values of Sn on illite IMt-1 in fresh ALLMR reference water (Meas=measured value).*

Chlorite (ripidolite) CCa-2

The sorption of tin on chlorite (ripidolite) CCa-2 from the Clay Mineral Society was determined in fresh ALLMR water (Figure Sn-13). The R_d values of Sn decrease as the pH increases. The experimental points form almost a straight line. The best estimate (BE) K_d values were taken from Figure Sn-13. The best estimate values for OLGA and OLGO waters (pH 5.8) were from pH 7.1. No extrapolation towards the acid pH range was made.

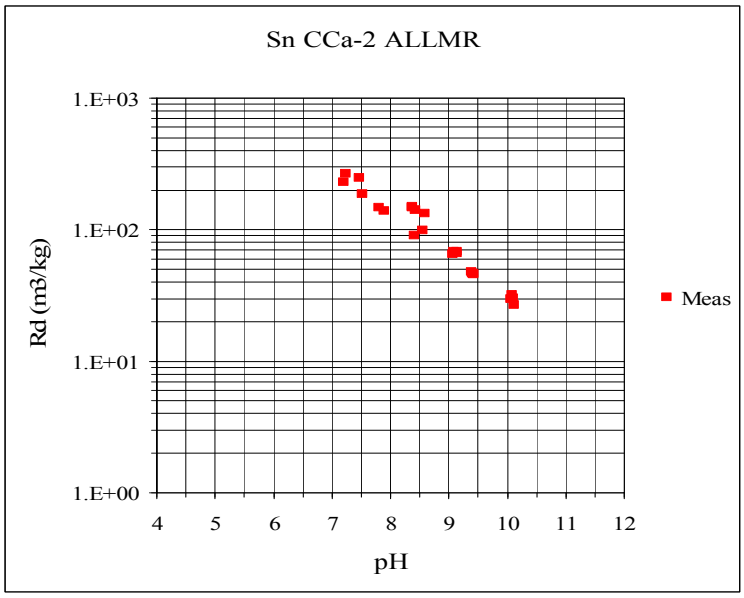

Figure Sn-13. *R_d values of Sn on chlorite (ripidolite) CCa-2 in fresh ALLMR reference water (Meas=measured value).*

18.3.2 Best estimate K_d values

The best estimate K_d values (m^3/kg) of tin for kaolinite, illite and chlorite in the reference waters are presented in Tables Sn-10 – Sn-12.

Table Sn-10. *The best estimate K_d (m^3/kg) values of tin for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+03**	**1.0E+03**	**1.0E+03**	**1.0E+03**	**1.0E+03**	**1.0E+03**	**1.0E+03**
10	1.0E+02	1.0E+02	1.0E+02	1.0E+02	1.0E+02	1.0E+02	1.0E+02

Table Sn-11. *The best estimate K_d (m^3/kg) values of tin for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**
10	9.0E+01	9.0E+01	9.0E+01	9.0E+01	9.0E+01	9.0E+01	9.0E+01

Table Sn-12. *The best estimate K_d (m^3/kg) values of tin for chlorite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Chlorite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.3E+02**	**2.3E+02**	**6.0E+01**	**1.8E+02**	**1.0E+02**	**2.0E+02**	**1.1E+02**
10.0	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01	3.0E+01

18.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(Sn-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Sn-2)}$$

The uncertainty factors are collected in Tables Sn-13, Sn-15 and Sn-17. Only those factors which are greater than one are listed.

Kaolinite

UF_{tot}= 7.2 the total uncertainty factor for ALLMR water and 8.0 for OLGA and OLGO waters. For other reference waters UF_{tot} is 10.

UF_{source}= 1.6. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for kaolinite were calculated. The factor 1.6 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1. Cation exchange capacity was not relevant here and so the factor is 1.

UF_{spec}= 1, the uncertainty of the speciation factor for ALLMR, OLGA and OLGO waters. The best estimate K_d values for kaolinite KGa-1b were calculated from the experimental R_d values of the ALLMR, OLGA and OLGO waters.

UF_{spec}= 1.4 for other reference waters as proposed in Hummel and Berner (2002).

UF_{pH}= 2.5. This uncertainty factor is used for the R_d values in OLGA and OLGO waters. The value corresponds to the high pH dependency of R_d values in OLGO.

UF_{pH}= 2.26 for other reference waters. The slope of the decrease of R_d values with increase of pH was about -1 for the part of R_d values where the anionic species becomes dominant in the OLGA and to Sn in Bradbury & Baeyens (2003). The accuracy of the determination of pH was taken to be 0.2 units, corresponding to an uncertainty of two to R_d value. Taking this uncertainty two times, the random error becomes 2.26. This value is used for waters for which experimental sorption data are not available.

$UF_{lab/field}$= 2. The conversion from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Sn for kaolinite in Olkiluoto are presented in Table Sn-14.

Illite

UF_{tot}= 3.6 the total uncertainty factor for ALLMR water and for other reference waters UF_{tot} is 5.1.

At pH 10 UF_{tot} is 5.5 for ALLMR water and 7.6 for other reference waters

Table Sn-13. *The factors used for calculation of the lower limit values for kaolinite in Olkiluoto geosphere. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite					
Water	UF_{source}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}
OLGA	1.6	1	2.5	2	8.0
OLGO	1.6	1	2.5	2	8.0
ALLMR	1.6	1	2.26	2	7.2
OLBA	1.6	1.4	2.26	2	10
OLSR	1.6	1.4	2.26	2	10
KR4	1.6	1.4	2.26	2	10
KR20	1.6	1.4	2.26	2	10

Table Sn-14. *The lower limit K_d (m^3/kg) values of tin for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.3E+02**	**1.3E+02**	**1.4E+02**	**1.0E+02**	**1.0E+02**	**1.0E+02**	**1.0E+02**
10	1.3E+01	1.3E+01	1.4E+01	1.0E+01	1.0E+01	1.0E+01	1.0E+01

UF_{source}= 1.4. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for illite were calculated. The factor 1.4 covers the scattering of the R_d values.
UF_{model}= 1. No model was used.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity (UF_{CEC}) covers the differences between the IMt-1 illite and natural illites.

UF_{spec}= 1 the uncertainty of speciation factor for ALLMR water. The best estimate K_d values for illite were calculated from the experimental R_d values of ALLMR water.

UF_{spec}= 1.4 for other reference waters as proposed in Hummel and Berner (2002).

UF_{pH}= 1. The uncertainty factor of pH on the R_d values for reference waters. A value of 1 is used for pH range 5.8 – 9.5 as there is no dependency of R_d values on pH. For pH values over 9.5, a value of 1.5 is used (for pH 10).

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Sn for illite in Olkiluoto are presented in Table Sn-16.

Table Sn-15. *The factors used for calculation of the lower limit values for illite in Olkiluoto geosphere. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
Water	UF_{source}	UF_{CEC}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}	UF_{tot} (pH 10)
OLGA	1.4	1.3	1.4	1 *	2	5.1	7.6
OLGO	1.4	1.3	1.4	1 *	2	5.1	7.6
ALLMR	1.4	1.3	1	1 *	2	3.6	5.5
OLBA	1.4	1.3	1.4	1 *	2	5.1	7.6
OLSR	1.4	1.3	1.4	1 *	2	5.1	7.6
KR4	1.4	1.3	1.4	1 *	2	5.1	7.6
KR20	1.4	1.3	1.4	1 *	2	5.1	7.6
* UF_{pH} = 1.5 at pH 10							

Table Sn-16. *The lower limit K_d (m^3/kg) values of tin for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.9E+01**	**2.9E+01**	**4.2E+01**	**2.9E+01**	**2.9E+01**	**2.9E+01**	**2.9E+01**
10	1.2E+01	1.2E+01	1.6E+01	1.2E+01	1.2E+01	1.2E+01	1.2E+01

Chlorite

UF_{tot}= 6.6 the total uncertainty factor for ALLMR water and for other reference waters UF_{tot} is 9.2.

UF_{source}= 1.4. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for illite were calculated. The factor 1.4 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity (UF_{CEC}) covers the differences between the CCa-2 chlorite and natural chlorites.

UF_{spec}= 1 the uncertainty of speciation factor for ALLMR water. The best estimate K_d values for illite were calculated from the experimental R_d values of ALLMR water.

UF_{spec}= 1.4 for other reference waters as proposed in Hummel and Berner (2002).

UF_{pH}= 1.8 the uncertainty factor of pH on the R_d values for reference waters.

$UF_{lab/field}$= 2. The upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Sn for chlorite in Olkiluoto are presented in Table Sn-18.

Table Sn-17. *The factors used for calculation of the lower limit values for chlorite in Olkiluoto geosphere. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Chlorite						
Water	UF_{source}	UF_{CEC}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}
OLGA	1.4	1.3	1.4	1.8	2	9.2
OLGO	1.4	1.3	1.4	1.8	2	9.2
ALLMR	1.4	1.3	1	1.8	2	6.6
OLBA	1.4	1.3	1.4	1.8	2	9.2
OLSR	1.4	1.3	1.4	1.8	2	9.2
KR4	1.4	1.3	1.4	1.8	2	9.2
KR20	1.4	1.3	1.4	1.8	2	9.2

Table Sn-18. *The lower limit K_d (m^3/kg) values of tin for chlorite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Chlorite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.5E+01**	**2.5E+01**	**9.1E+00**	**2.0E+01**	**1.1E+01**	**2.2E+01**	**1.2E+01**
10	3.3E+00	3.3E+00	4.5E+00	3.3E+00	3.3E+00	3.3E+00	3.3E+00

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19 AMERICIUM, CURIUM AND LANTHANIDES (III)

19.1 Speciation

Americium Am (III) and curium Cm (III) are similar actinide elements in their environmental chemistry. In the conditions concerned, their oxidation state is solely +III. The sorption values determined for Am are also used for Cm. Owing to their chemical similarities, the lanthanide Ln (III) ions are often used instead of Am in sorption studies. In this work the mass distribution ratio of sorption (K_d) of Am and Cm is calculated from experimental data for Eu.

Speciation of americium and europium in the groundwaters was evaluated by modelling calculations using the Thermo_Chimie 7b database (ANDRA 2009). The species of Am and Eu are almost the same at lower pH. At higher pH, Eu is hydrolysed at slightly lower pH than Am. In fresh ALLMR, brackish OLBA and saline OLSR waters, the Am and Eu hydroxysilicato complexes dominate in the neutral pH range (Figures Am-1 – Am-3, and Figures Eu-1 – Eu-4).

In the glacial melting water OLGA, at around pH 6, the main species is the Am^{3+} ion. Speciation in ALLMR and OLSR at the neutral pH region is almost the same, and the main species is the cationic silicate complex. In OLBA, the relatively high carbonate concentration is followed by the result that at the relevant pH range: the concentration of the cationic carbonate complex is the same as that of the hydroxy silicate complex. At higher pH in ALLMR and OLSR, the hydroxy complexes are the most abundant. In OLBA, the anionic carbonate complexes are important in the high pH region. At pH 10, the impact of these, presumably non-sorbing, species is about 50 % (Figure Am-2).

The natural fresh groundwater KR4_81_1 and brackish water KR20_465_1 both have high carbonate concentrations. The increase of pH is followed by the precipitation of calcite in these waters. Modelling of Eu in these waters indicates that the fraction of hydroxy complexes is very low at the pH of the waters between pH 7 and 8 (Figures Eu-5 and Eu-6). The higher calcium concentration in KR20_465_1 suppresses the carbonate concentration at pH 10 to a low level, and in this water the hydroxo complexes are the most abundant. In KR4_81_1, the hydroxo complexes are at a very low level at pH 10.

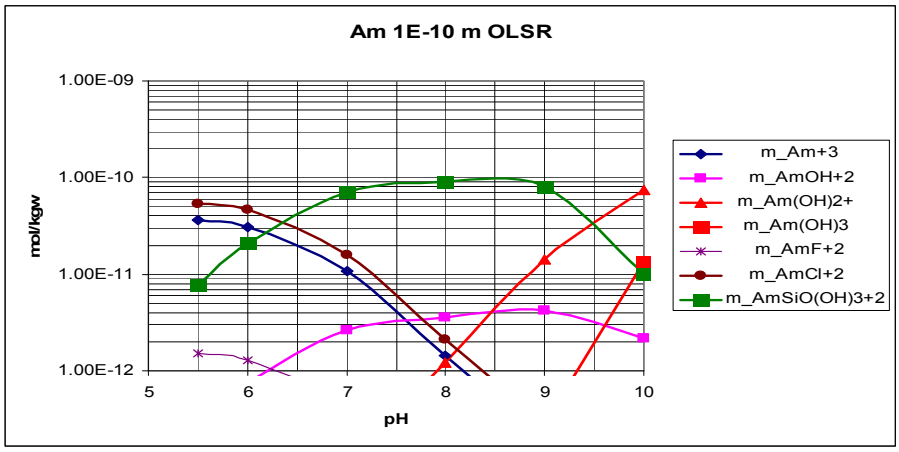

Figure Am-1. *Speciation of Am in CO_2 free saline OLSR water.*

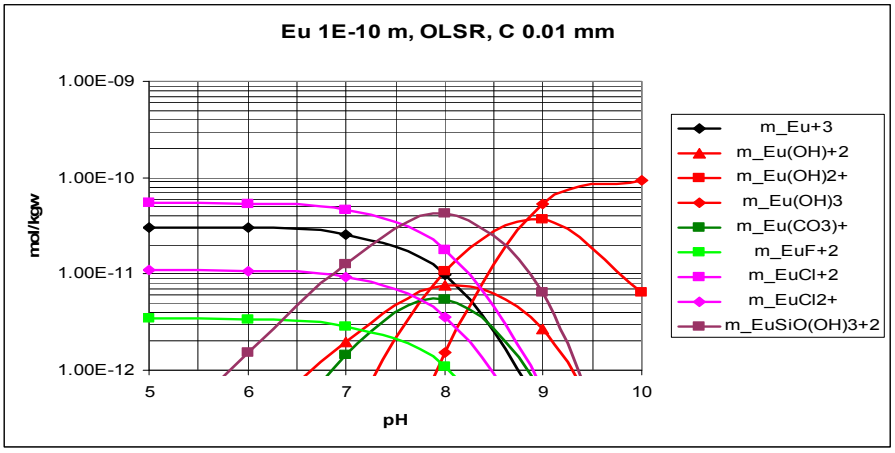

Figure Eu-1. *Speciation of Eu in saline OLSR water.*

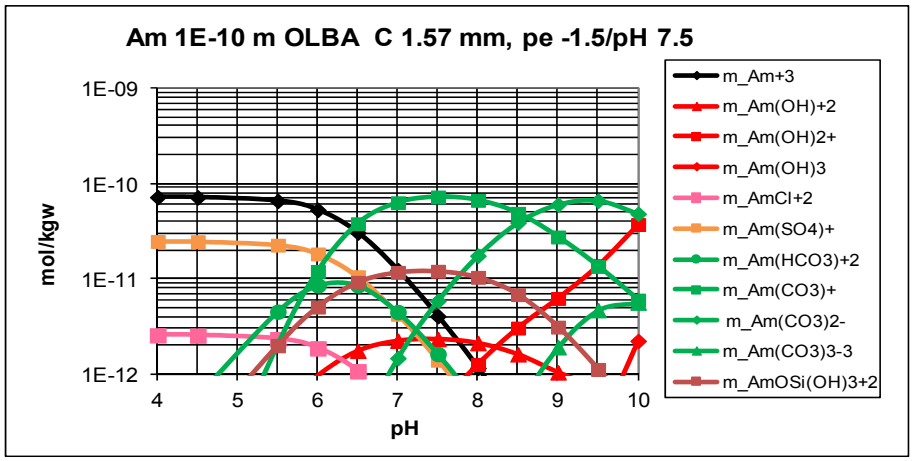

Figure Am-2. *Speciation of Am in brackish OLBA water.*

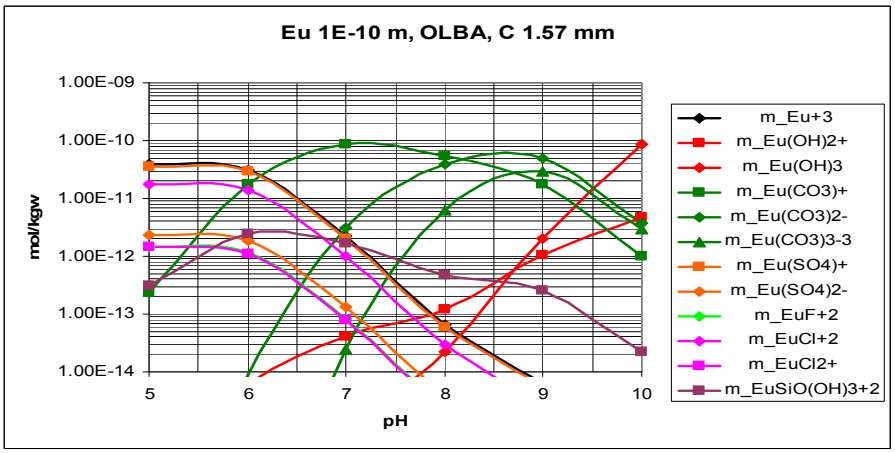

Figure Eu-2. *Speciation of Eu in brackish OLBA water.*

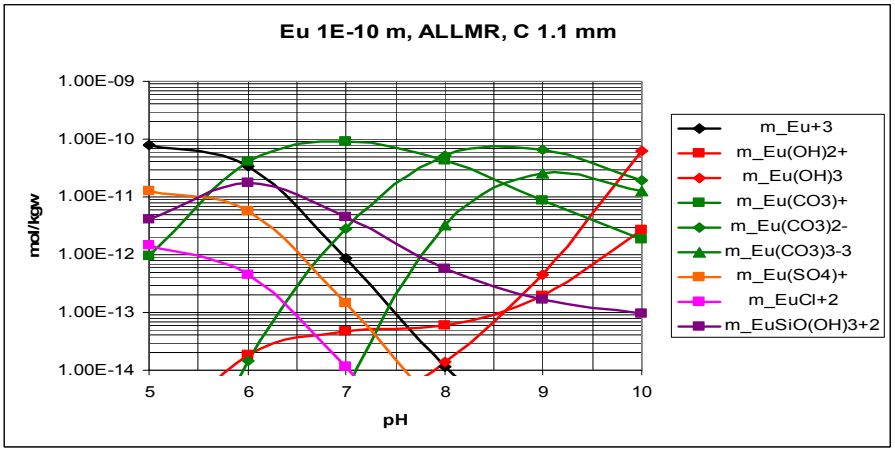

Figure Eu-3. *Speciation of Eu in fresh ALLMR water with 1.1 mm carbonate concentration.*

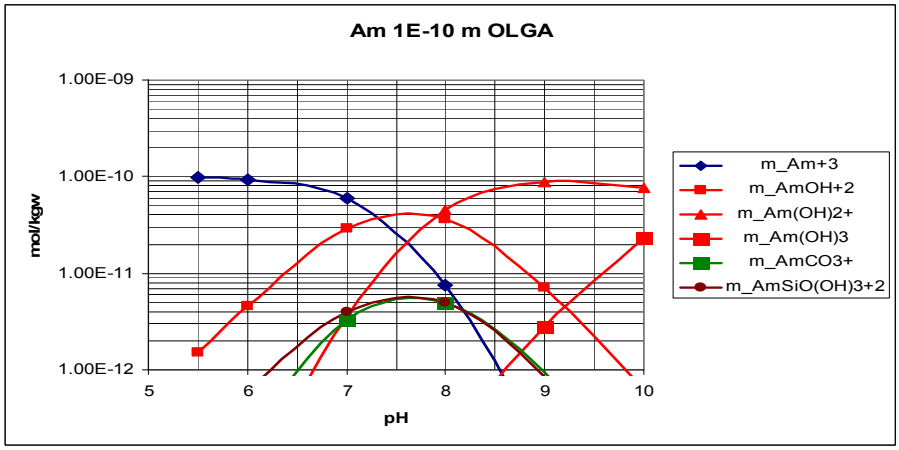

Figure Am-3. *Speciation of Am in glacial OLGA water.*

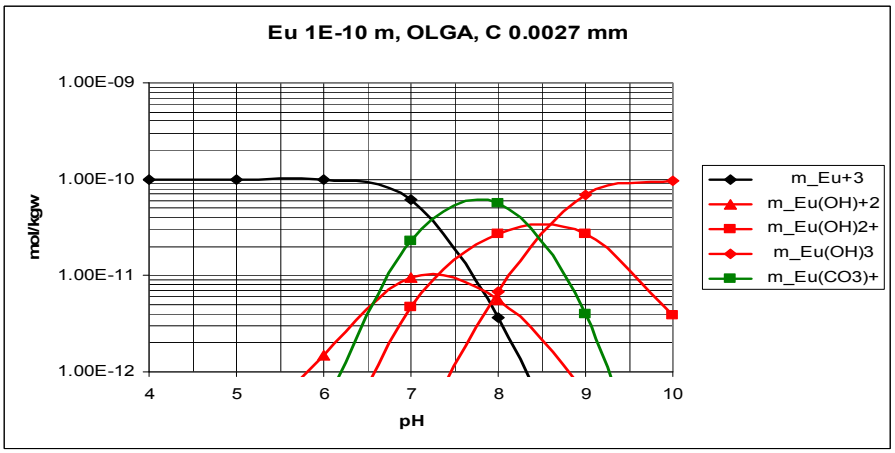

Figure Eu-4. *Speciation of Eu in glacial OLGA water.*

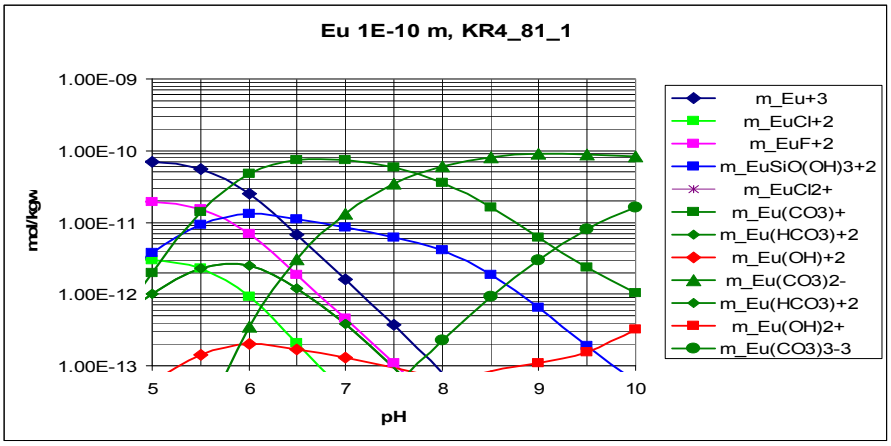

Figure Eu-5. *Speciation of Eu in brackish KR4_81_1 water.*

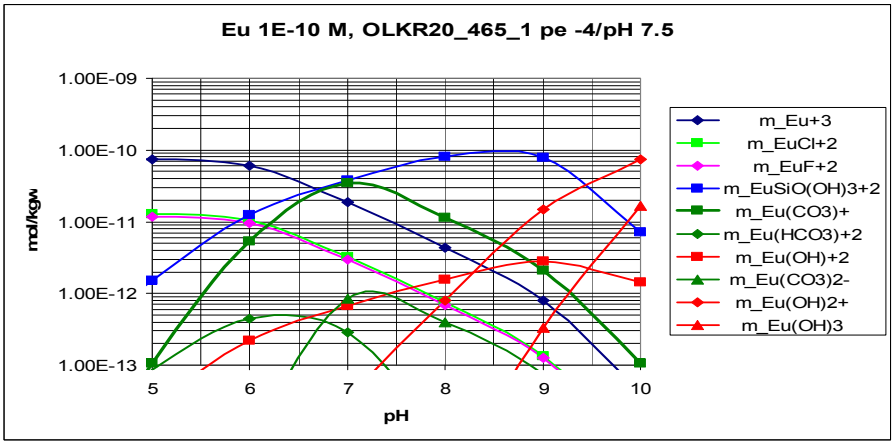

Figure Eu-6. *Speciation of Eu in saline KR20_465_1 water.*

19.2 Sorption on rocks

In the modelling of sorption in a carbonate-free solution using a non-electrostatic surface complexation model (Bradbury & Baeyens 2009), only the hydroxo complexes were taken into account. Fernandes et al. (2008) modelled sorption of Eu on montmorillonite in carbonate-containing solutions by also adopting Eu hydroxy carbonato surface complexes. Possible effects of Eu-hydoxysilicato complex on sorption is assumed to already be affecting the sorption data.

19.2.1 Source data

Sorption of Am and Eu on granitic rocks takes place mainly on minerals with high cation exchange capacity and large surface area such as micas. Puukko et al. (in Olin et al. 2008) determined the sorption of Eu (III) on crushed Olkiluoto granodiorite (OLA) and mica gneiss (OLB) in the carbonate-free modification of ALLMR and in saline OLSR waters. The R_d values for the reference rocks in the experimental solutions were

converted from the R_d data of OLB (mica gneiss) and OLA (granodiorite) using the concentration of micaceous minerals and hornblende in the rocks as the scaling factor. K_d values in the experimental pH values in the solutions were further obtained by conversion of the R_d values for crushed rock to K_d for intact rocks (Table Eu-1). The K_d values in the ALLMR and OLSR waters at the pH of 8.8 (ALLMR) and pH 8.3 (OLSR) were obtained by using the pH dependence of sorption to biotites and illite (Table Eu-2).

The sorption on biotites of the rocks in $NaClO_4$ solutions (Figures Eu-7 and Eu-8) was also determined and indicate that sorption depends on the pH and ionic strength of the solution. The results are in agreement with the sorption of Eu on illite in Poinssot et al. (1999). The results are needed for the conversion of source data for rocks to K_d values in the reference waters.

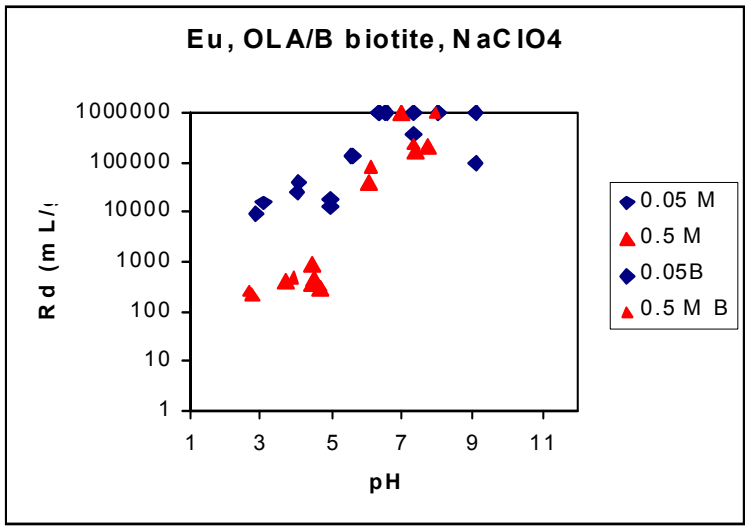

Figure Eu-7. *R_d values of Eu on Olkiluoto biotites in 0.05 M and 0.5 M $NaClO_4$ solutions (Olin et al. 2008).*

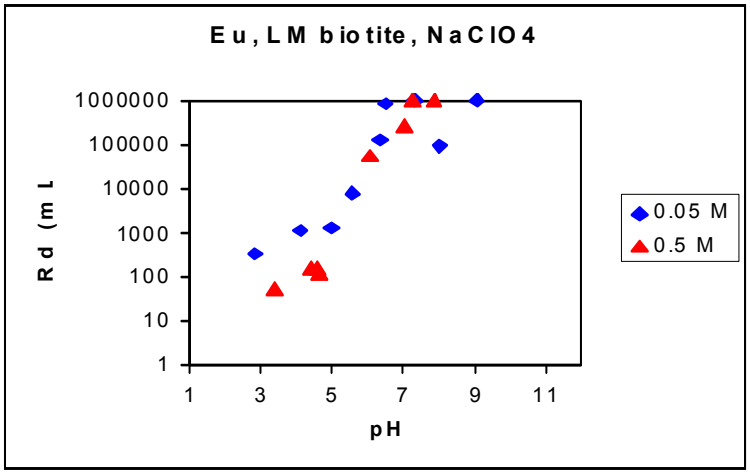

Figure Eu-8. *R_d values of Eu on ground pegmatitic biotite in 0.05 M and 0.5 M $NaClO_4$ solutions (Olin et al. 2008).*

Table Eu-1. *R_d values (m^3/kg) of Eu for the source data rocks and calculated K_d values (m^3/kg) of Eu for the reference rocks in the experimental ALLMR and OLSR type waters from R_d values in OL mica-gneiss and OL-granodiorite (Olin et al. 2010).*

SD rock	water	pH	Rd	T-MGN	P-TGG	T-TGG	PGR
granodiorite	ALLMR	6.4	2.5	0.770	0.354	0.148	0.030
granodiorite	ALLMR	6.6	5.1	1.56	0.720	0.300	0.061
granodiorite	OLSR	8.5	15	4.60	2.12	0.885	0.181
mica gneiss	ALLMR	6.9	7.0	1.308	0.630	0.252	0.051
mica gneiss	ALLMR	7	5.5	1.028	0.491	0.198	0.040
mica gneiss	OLSR	7.3	9.9	1.850	0.391	0.356	0.073
mica gneiss	OLSR	7.4	6.3	1.177	0.249	0.226	0.046
SD = source data rock							

Table Eu-2. *K_d values (m^3/kg) of Eu for the reference rocks at pH of carbonate-free ALLMR and OLSR waters calculated from K_d values in Table Eu-1.*

SD rock	water	pH	T-MGN	P-TGG	T-TGG	PGR
granodiorite	ALLMR	8.8	3.08	1.42	0.59	0.12
granodiorite	ALLMR	8.8	6.26	2.88	1.20	0.25
granodiorite	OLSR	8.3	4.6	2.12	0.88	0.18
mica gneiss	ALLMR	8.8	2.62	0.55	0.50	0.10
mica gneiss	ALLMR	8.8	2.06	0.43	0.40	0.08
mica gneiss	OLSR	8.3	1.85	0.39	0.36	0.07
mica gneiss	OLSR	8.3	1.18	0.25	0.23	0.05
SD rock = source data rock						

19.2.2 Best estimate K_d values

Speciation calculations of Eu and Am indicated that, in addition to hydroxo complexes, carbonate and hydroxysilicato complexes are present in the groundwaters. Carbonate complexation does not reduce sorption at pH lower than pH 8, as shown by the same sorption of Eu on montmorillonite in Fernandes et al. (2008) in $NaClO_4$ solutions under carbonate-free and ambient atmospheric conditions. The results further indicate that the anionic Eu-dicarbonato complex is practically non-sorptive. It follows that only in ALLMR water (pH 8.8) may the anionic carbonate complexation lower the sorption.

The ALLMR and OLSR waters both contain silicate, so the effect of hydroxysilicato complexation on sorption is included in the experimental results. In KR20_465_1 water, this complex is the dominating (60 %) species. The difference between OLSR and KR20_465_1 waters is, however, not large and as the best estimate the sorption in KR20_465_1 is calculated from K_d value for OLSR.

Sorption of Eu on the biotites (Olin et al. 2008) and on kaolinite (Puukko & Hakanen 2001, 2004) and illite (Poinssot et al. 1999) show that at pH 7–10 the sorption is high

and the same within the accuracy of the determinations. In the glacial water OLGA (pH 5.8), the sorption is lower than in other reference waters.

In OLGA water at pH 5.8, the Eu^{3+} is the main species, and in ALLMR water at pH 6.4 the Eu^{3+} ion and the cationic carbonato complex comprise 90% of the species. Also, the hydroxysilicato complex (10 %) is cationic and is assumed sorptive. The increase of R_d values for biotite and in 0.01 M $NaClO_4$ between pH 5 and 7 in Poinssot et al. (2009) has a slope of about 3-5/pH unit. Owing to the fact that extrapolation from the experimental data to rocks is made, the K_d value for OLGA is here conservatively calculated by dividing the K_d value for ALLMR at pH 6.4 by 5. Due to lack of data, the lower ionic strength of OLGA could not be taken into account.

The K_d values in ALLMR water (pH 8.8) are calculated from the value at pH 7 in the carbonate-free experimental solution. A conversion factor of 4 was estimated for R_d values between pH 7 and pH 8.8. The proportion of the non-sorptive anionic dicarbonato complex is 20 % at pH 8.8.

The K_d values in brackish waters KR4_81_1, OLBA and KR20_465_1 are calculated from the value of the mean of T-MGN (3.02 m^3/kg) in ALLMR and OLSO waters by estimating that the anionic dicarbonato complex is non-sorptive. Values for the other rocks should be in proportion to T-MGN by their content and accessibility of micaceous minerals. The values, especially for the low-mica rocks in Table Eu-2, are proportionally lower than the mica contents in the different rocks suggest. This is probably due to the fact that the mica+hornblenede contents of the source data rocks were higher than those of T-TGG and PGR. Nevertheless, the mean values calculated for these rocks are proposed as the best estimate values. For P-TGG, the accessibility of sorption sites is assumed to be 50 %. The best estimate K_d values are given in Table Eu-3.

At pH 10 the anionic dicarbonato complex is the main species in KR4_81_1 water. The fraction of sorptive species is only 0.015. In the other waters, the fraction is 0.9 or higher. The best estimate K_d values at pH 10 are given in Table Eu-3.

Table Eu-3. *Best estimate K_d values of Eu on the reference conditions and at pH 10. KR4 = KR4_81_1; KR20 = KR20_465_1.*

	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
pH	5.8	8.8	8.3	7.6	7.8	7.4
FSS	1.00	0.80	1.00	1.00	0.50	0.95
T-MGN	0.15	2.4	3.0	3.0	3.0*	3.0*
P-TGG	0.07	1.2	1.5	1.5	1.5*	1.5*
T-TGG	0.03	0.5	0.58	0.58	0.58*	0.58*
PGR	0.006	0.09	0.11	0.11	0.11*	0.11*
	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
pH	10	10	10	10	10	10
FSS	1.00	>0.90	>0.90	0.90	0.015	>0.90
T-MGN	3	2.7	2.7	2.7	0.045	2.7
P-TGG	1.1	1.0	1.0	1.0	0.015	1.0
T-TGG	0.6	0.5	0.5	0.5	0.008	0.5
PGR	0.1	0.1	0.1	0.1	0.0015	0.1
FSS fraction of sorptive species * experimental sorption to montmorillonite suggests no reduction in sorption by the carbonate concentration in the water						

Am, Cm

Sorption of Eu and Am on kaolinite (Puukko & Hakanen 2001) was almost the same. It is proposed that the best estimate K_d values of other Ln (III) (Sm) lanthanides and An(III) (Am, Cm) actinides for reference rocks are the same as for Eu in the same chemical conditions.

Table Eu-4. *The best estimate K_d (m^3/kg) values of Am, Cm, and Ln (III) for mica gneiss T-MGN in the reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-01**	**1.5E-01**	**2.4E+00**	**3.0E+00**	**3.0E+00**	**3.0E+00**	**3.0E+00**
10	3.0E+00	3.0E+00	2.7E+00	2.7E+00	2.7E+00	4.5E-02	2.7E+00

Table Eu-5. *The best estimate K_d (m^3/kg) values of Am, Cm, and Ln (III) for P series granodiorite gneiss P-TGG in the reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E-02**	**7.0E-02**	**9.0E-01**	**1.1E+00**	**1.1E+00**	**1.1E+00**	**1.1E+00**
10	1.1E+00	1.1E+00	1.0E+00	1.0E+00	1.0E+00	1.5E-02	1.0E+00

Table Eu-6. *The best estimate K_d (m^3/kg) values of Am, Cm, and Ln (III) for T series granodiorite gneiss T-TGG in the reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-02**	**3.0E-02**	**5.0E-01**	**5.8E-01**	**5.8E-01**	**5.8E-01**	**5.8E-01**
10	6.0E-01	6.0E-01	5.0E-01	5.0E-01	5.0E-01	8.0E-03	5.0E-01

Table Eu-7. *The best estimate K_d (m^3/kg) values of Am, Cm, and Ln (III) for pegmatitic granite PGR in the reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**6.0E-03**	**9.0E-02**	**1.1E-01**	**1.1E-01**	**1.1E-01**	**1.1E-01**
10	1.0E-01	1.0E-01	1.0E-01	1.0E-01	1.0E-01	1.5E-03	1.0E-01

19.2.3 Lower limit K_d values

The uncertainty factor covers both the mineralogical and chemical uncertainties in solutions. The lower limit K_d value is calculated by dividing the best estimate value by the uncertainty factor. The factors for rocks are presented in Table Eu-8.

The increase of R_d with pH is typical for surface complexation and the high pH dependency of the K_d values is the main source of uncertainty. For Eu, the amount of sorption data is scarce. The sorption data used for backing up the pH dependency and complexation behaviour suggest that the main solution chemical uncertainty is at the pH of the sorption edge, e.g. for K_d to OLGA. A conservative factor was used in extrapolation. The uncertainty consists of uncertainties in the source data and in the calculation of the K_d values. The contribution of the speciation of Eu in OLGA and OLBA is different from that in ALLMR and OLSR, for which sorption data are available. This is an additional source of uncertainty. In the calculation of the best estimate values for OLGA and OLBA, care was taken not to overestimate the K_d values. The chemical uncertainty factor originates from the extrapolation to pH values from the source data to the reference waters. The uncertainty in value of the R_d/pH slope is covered by a factor of 2. Uncertainty due to the fact that the source data waters were CO_2-free was taken into account by assuming that the dicarbonato complexes are totally non-sorbing. The differences in speciation are covered by a factor of 1.4, as with clays. The chemical uncertainty is thus covered by a factor of 2.8. The mica+hornblende contents of the source data mica gneiss was higher than in the reference rocks, and the content in source data granodiorite only a little less. It followed that conversion of source data R_d values to reference rock R_d data most likely yielded low values. It remains the case that the largest mineralogical uncertainty comes from the conversion of R_d data for crushed rock to K_d for intact rock. This is covered by a factor of 7. For T-TGG and PGR, the conversion from source data to these rocks yielded relatively lower values than for T-MGN and P-TGG. For these rocks, the mineralogical uncertainty factor used also covers the chemical uncertainty. The total uncertainty factors are given in Table Eu-8.

Table Eu-8. *Uncertainty factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	20
P-TGG	20
T-TGG	20
PGR	50

Table Eu-9. *The lower limit K_d (m^3/kg) values of Am, Cm, and Ln (III) for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-03**	**7.5E-03**	**1.2E-01**	**1.5E-01**	**1.5E-01**	**1.5E-01**	**1.5E-01**
10	1.5E-01	1.5E-01	1.4E-01	1.4E-01	1.4E-01	2.3E-03	1.4E-01

Table Eu-10. *The lower limit K_d (m^3/kg) values of Am, Cm, and Ln (III) for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.5E-03**	**3.5E-03**	**4.5E-02**	**5.5E-02**	**5.5E-02**	**5.5E-02**	**5.5E-02**
10	5.5E-02	5.5E-02	5.0E-02	5.0E-02	5.0E-02	7.5E-04	5.0E-02

Table Eu-11. *The lower limit K_d (m^3/kg) values of Am, Cm, and Ln (III) for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-03**	**1.5E-03**	**2.5E-02**	**2.9E-02**	**2.9E-02**	**2.9E-02**	**2.9E-02**
10	3.0E-02	3.0E-02	2.5E-02	2.5E-02	2.5E-02	4.0E-04	2.5E-02

Table Eu-12. *The lower limit K_d (m^3/kg) values of Am, Cm, and Ln (III) for pegmatitic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.2E-04**	**1.2E-04**	**1.8E-03**	**2.2E-03**	**2.2E-03**	**2.2E-03**	**2.2E-03**
10	2.0E-03	2.0E-03	2.0E-03	2.0E-03	2.0E-03	3.0E-05	2.0E-03

19.3 Sorption on clays

19.3.1 Source data

Speciation of Eu and Am in the groundwaters was discussed earlier. In addition to hydroxo complexes, the Eu hydroxysilicato and carbonato complexes are present in the reference waters.

19.3.2 Best estimate K_d values

Kaolinite

Sorption in $NaNO_3$ solution

Sorption of Eu on conditioned KGa-1b kaolinite was determined under an argon atmosphere in 0.05, 0.1 and 0.5 M $NaNO_3$ solutions at pH 3-9 (Puukko & Hakanen 2004, Figure 4) and sorption of Eu and Am on conditioned kaolinite in 0.001, 0.01 and 0.1 M $NaNO_3$ (Puukko & Hakanen 2001, Figure 9). At pH 3-8, higher sorption was measured in lower ionic strength solutions. Sorption of Eu and Am was the same or little higher than for Am. The R_d value in the glacial water OLGA is based on sorption in 0.05 M $NaNO_3$ solution. Values for brackish waters (pH 7.6 and 7.8) are based on sorption in 0.1 M $NaNO_3$ and the value for KR20_465_1 on sorption in 0.5 M $NaNO_3$. The pH of OLGA (5.8), KR20_465_1 (pH 7.4), OLBA (pH 7.6) and KR4_81_1 (pH 7.8) are at the pH region of increase of sorption with increasing pH. At the pH of the other waters (ALLMR. OLSR), the R_d values were levelled out so that no differences could be seen as a function of pH or ionic strength. The same R_d value can be selected from pH 8 to pH 10 in carbonate-free conditions for all waters.

The sorption pH edge of Am and Pu (III) measured by Buda et al. (2008) was almost the same under air and argon atmospheres in humics-containing solutions, indicating similar chemical behaviour of these An(III) actinides.

Eu-hydroxysilicato complex

The proportion of the Eu-hydroxysilicato complex is highest (60%) in KR20_465_1 water. Soluble silicates capable of forming this complex are most likely present in all sorption experiments performed to aluminosilicate minerals, as exemplified by the solution analysis results in Poinssot et al. (1999). As the best estimate, the cationic Eu-hydroxysilicato complex is assumed to be sorptive.

Carbonate complexation

Sorption on Na-montmorillonite was determined in both inert and ambient atmospheres and 20 mM TIC in 0.1 M $NaClO_4$ solution at pH 4-10 (Fernandes et al. 2008). Sorption under ambient carbonate partial pressure at high pH decreases strongly with an increase of pH when the anionic bicarbonate complex becomes the main species. Under an ambient atmosphere, sorption was reduced only at a pH higher than pH 8. At lower pH, the sorption is even slightly higher than in inert atmospheric conditions. Formation of ternary carbonato surface complexes under ambient atmospheric conditions has also

been regarded as possible on kaolinite (Stumpf et al. 2002, 2004). The dependence of sorption on carbonate concentration was most probably due to speciation of Eu in the solutions. The same behaviour is assumed in sorption on other clays.

Based on the results in Fernandes et al. (2008) for OLGA, ALLMO, OLSR and OLKR20, no correction for carbonate must be made to the R_d values. In the higher carbonate waters OLBA and KR4_81_1 (pH 7. 6 and pH 7.8), the calculated speciation is, compared to ALLMR water, more dependent on hydroxysilicato complexation than on carbonate complexation. Only to sorption in ALLMR (pH 8.8), is a reduction of R_d value due to carbonato complexation made. At pH 10, the high carbonate concentration in KR4 is followed by the assumption that the dicarbonato complexes are the main species, and sorption is reduced for this.

Best estimate K_d values for Eu, and trivalent actinides

Best estimate K_d values for Eu and Am are given in Tables Eu-15 and Am-1. For Am at pH 5.8, the source data indicate the same sorption as for Eu. Note that for KR4_81_1 water, the speciation calculation suggests that the fraction of the anionic carbonato complex is 0.50 and in KR20_465_1 it is 0.05. The experimental values in Fernandes et al. (2008), however, show that no reduction in sorption was found at pH lower than pH 8.

At pH 10 in the KR4_81_1 water, the amount of the anionic Eu-bicarbonato complex is high and the fractions of the hydroxo complexes and the cationic carbonato complex are together only 0.015. Therefore, in KR4_81_1 at pH 10 the K_d value is proposed to be 0.015 times that in carbonate-free conditions. In the other reference waters, the speciation is dominated (>90%) by hydroxo complexes or cationic carbonato complexes.

Table Eu-13. *R_d values (m^3/kg) of Eu for kaolinite in carbonate-free conditions, fraction of sorptive species and the K_d values (m^2/kg) of Eu in the groundwaters and at pH 10. KR4 = KR4_81_1 KR20 = KR20_465_1.*

Kaolinite						
	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
pH	5.8	8.8	8.3	7.6	7.8	7.4
FSS	1.00	0.80	1.00	1.00	0.50	0.95
R_d	5	600	600	300	300	30
K_d	5	480	600	300	300*	30*
	OLGA	ALLMR	OLSR	OLBA	KR4	KR20
pH	10	10	10	10	10	10
FSS	1.00	>0.90	>0.90	0.90	0.015	>0.90
R_d	600	600	600	600	600	600
K_d	600	540	540	540	9	540
FSS = fraction of sorptive species * experimental sorption values propose no reduction due to carbonate complexation						

Illite

Sorption in $NaClO_4$ solution

Sorption of Eu has been determined in 0.01 M and 0.1 M $NaClO_4$ solutions at pH 3–11 under an inert CO_2-free atmosphere in Poinssot et al. (1999), and for Am (Figure 1b) in Bradbury & Baeyens (2009). The sorption edges for Eu and Am are identical. At pH of relevance for the groundwaters, the sorption was the same in the 0.01 M and 0.1 M solutions. These data were adopted as the source data for sorption of Ln(III), Am(III) and Cm(III). Bradbury & Baeyens (2009) also included a graph (Figure 2a) of sorption of Am on Na-illite by Gorgeon (1994). The data by Bradbury & Baeyens (2009) was preferred due to the fact that the original data by Gorgeon was not accessible to the authors of this report. The dependence of Eu sorption on carbonates in the waters was derived from the results of sorption of Eu on Na-montmorillonite in an inert atmosphere, ambient atmosphere and 20 mM TIC (total inorganic carbon) in 0.1 M $NaClO_4$ solution at pH 4–10 in Fernandes et al. (2008).

For Eu and Am, the same R_d value can be selected from pH 7 to pH 10 under carbonate-free conditions. At pH 5.8 (OLGA) the R_d value is lower. The main species in the waters are free Eu^{3+} and Am^{3+} cations and Eu/Am carbonate complexes. In saline waters the cationic hydroxysilicato complex is also present.

Eu-hydroxysilicato complexation

According to the Thermo_Chimie database, the Eu-hydroxysilicato complexes are the major species in KR20_465_1 water. Silicates are inherently present in experiments performed using silicate minerals, as also indicated by solution conditions in Poinssot et al. (1999). Modelling of sorption values in Poinssot et al. (1999) in 0.1 M $NaClO_4$ has been made by assuming that in the solution only Eu^{3+} and Eu-hydroxo complexes are the sorption determining species. The role of Eu-hydroxysilicato complexes in sorption is not clear. As the best estimate, the Eu-hydroxysilicato complex is assumed to be sorptive, as was assumed for the hydroxysilicato complexes of Th.

Table Eu-14. *The R_d values (m^3/kg) of Eu for illite in carbonate-free conditions, fraction of sorptive species and the K_d values (m^3/kg) of Eu in the groundwater and at pH 10.*

Illite						
	OLGA	ALLMR	OLSR	OLBA	KR4	KR_20
pH	5.8	8.8	8.3	7.6	7.8	7.4
FSS	1.00	0.80	1.00	1.00	0.50	0.95
R_d	250	250	250	250	250	250
K_d	250	200	250	250	250*	250*
	OLGA	ALLMR	OLSR	OLBA	KR4	KR_20
pH	10	10	10	10	10	10
FSS	1.00	>0.90	>0.90	0.90	0.015	>0.90
R_d	250	250	250	250	250	250
K_d	250	225	225	225	4	225
FSS = fraction of sorptive species * experimental sorption values show no reduction due to carbonato complexation						

Table Am-1. *The R_d values (m^3/kg) of Am for illite in carbonate-free conditions, fraction of sorptive species and the K_d values (m^3/kg) of Am in the groundwater and at pH 10.*

Illite						
	OLGA	ALLMR	OLSR	OLBA	KR4_81_1	KR_20_465
pH	5.8	8.8	8.3	7.6	7.8	7.4
FSS	1.00	0.80	1.00	1.00	0.50	0.95
R_d	100	250	250	250	250	250
K_d	100	200	250	250	250 *	250*
	OLGA	ALLMR	OLSR	OLBA	KR4_81_1	KR_20_465
pH	10	10	10	10	10	10
FSS	1.00	>0.90	>0.90	0.90	0.015	>0.90
R_d	250	250	250	250	250	250
K_d	250	225	225	225	4	225
FSS = fraction of sorptive species * experimental sorption values show no reduction due to carbonato complexation						

Table Eu-15. *The best estimate K_d (m^3/kg) values of Am, Cm, and Ln (III) for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E+00**	**5.0E+00**	**4.8E+02**	**3.0E+02**	**6.0E+02**	**3.0E+02**	**3.0E+01**
10	6.0E+02	6.0E+02	5.4E+02	5.4E+02	5.4E+02	9.0E+00	5.4E+02

Table Eu-16. *The best estimate K_d (m^3/kg) values of Am, Cm, and Ln (III) for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+02**	**1.0E+02**	**2.0E+02**	**2.5E+02**	**2.5E+02**	**2.5E+02**	**2.5E+02**
10	2.5E+02	2.5E+02	2.3E+02	2.3E+02	2.3E+02	4.0E+00	2.3E+02

19.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source}*UF_{model}*UF_{CEC}*UF_{spec}*UF_{pH}*UF_{lab/field} \quad (1)$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\ (LL) = K_d(BE)/UF_{tot} \quad (2)$$

The uncertainty factors are collected in Tables Eu-17 and Eu-19. Only those factors which are greater than one are listed.

Kaolinite

The total uncertainty factor UF_{tot} varies from 9.1 to 29.

UF_{source}= 2.5. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for kaolinite were calculated. The factor 2.5 covers the measured R_d values for Eu and Am being lower than those selected as the best estimate R_d values in carbonate-free conditions.

UF_{model}= 1. No model was used.

UF_{CEC}= 1.3. The uncertainty of cation exchange capacity (UF_{CEC}) is accepted as 1.3.

UF_{spec}= 1.4. The uncertainty of speciation (UF_{spec}) is 1.4 for OLGA (pH 5.8), ALLMR, KR4, OLSR, OLBA at pH 7-8.8 waters.

UF_{spec}= 2 for KR20 water at pH 7.4 owing to uncertainties in the sorptivity of Eu-hydroxy silicato complexes.

UF_{spec}= 1.4 for all reference waters at pH 10.

UF_{pH}= 2.26. The effect of pH on the R_d values (UF_{pH}) is 2.26 for OLGA, OLBA, OLKR4, KR20 waters.

UF_{pH}= 1 for OLSR, ALLMR waters.

$UF_{lab/field}$= 2. The uncertainty of upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Eu for kaolinite in the Olkiluoto geosphere are presented in Table Eu-18.

Table Eu-17. *The factors used for calculation of the lower limit values for kaolinite in the Olkiluoto geosphere. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	UF_{CEC}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}
OLGA	1.3	1.4	2.26	2	21
OLGO	1.3	1.4	2.26	2	21
ALLMR	1.3	1.4	1	2	9.1
OLBA	1.3	1.4	2.26	2	21
OLSR	1.3	1.4	1	2	9.1
KR4	1.3	1.4	2.26	2	21
KR20	1.3	2 *	2.26	2	29
* owing to uncertainties in sorptivity of Eu-hydroxysilicato complex.					

Table Eu-18. *The lower limit K_d (m^3/kg) values of Am, Cm, and Ln (III) for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.4E-01**	**2.4E-01**	**5.3E+01**	**1.4E+01**	**6.6E+01**	**1.4E+01**	**1.0E+00**
10	2.9E+01	2.9E+01	5.9E+01	2.6E+01	5.9E+01	4.3E-01	2.6E+01

Illite

The total uncertainty factor UF_{tot} varies from 5.4 to 12.

UF_{source}= 1.6. The uncertainty factor of the source data (UF_{source}) describes the uncertainty of the experimental R_d values, from which the best estimate K_d values for kaolinite were calculated. The factor 1.6 covers the measured R_d values for Eu and Am being lower than those selected as the best estimate R_d values in carbonate-free conditions.

UF_{model}= 1. No model was used.

UF_{CEC}= 1.3. The cation exchange capacity (CEC) for illite is generally higher than for kaolinite. The uncertainty in the source material compared with the Olkiluoto site illite

is taken into account in the uncertainty factor UF_{CEC} which was taken as 1.3, since the CEC of the source data illite and the Olkiluoto illite may be significantly different (Bradbury & Baeyens 2003c, Missana et al. 2008).

UF_{spec}= 1. The uncertainty of speciation (UF_{spec}) is 1 for OLGA (pH 5.8) water.

UF_{spec}= 1.3 for ALLMR, KR4, OLSR, OLBA (pH 7-8.8) waters.

UF_{spec}= 2 for KR20 water at pH 7.4 owing to uncertainties in the sorptivity of the Eu-hydroxy silicato complexes.

UF_{spec}= 1.3 for all reference waters at pH 10.

UF_{pH}= 2.26. The effect of pH on the R_d values (UF_{pH}) is 2.26 for OLGA, because the R_d of Am is at the sorption pH edge and the R_d value of Eu is near the upper part of the pH edge.

UF_{pH}= 1 at pH 7-10 for OLSR, ALLMR, OLBA, KR4, KR20 waters.

$UF_{lab/field}$= 2. The uncertainty of upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Eu for illite in the Olkiluoto geosphere are presented in Table Eu-20.

Table Eu-19. *The factors used for calculation of the lower limit values for illite in the Olkiluoto geosphere. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
Water	UF_{source}	UF_{CEC}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}	UF_{tot} pH10
OLGA	1.6	1.3	1 *	2.26	2	9.4	12
OLGO	1.6	1.3	1 *	2.26	2	9.4	12
ALLMR	1.6	1.3	1.3	1	2	5.4	5.4
OLBA	1.6	1.3	1.3	2.26	2	12	12
OLSR	1.6	1.3	1.3	1	2	5.4	5.4
KR4	1.6	1.3	1.3	2.26	2	12	12
KR20	1.6	1.3	2 *	2.26	2	19	12
* UFspec is 1.3 for all reference waters at pH 10							

Table Eu-20. *The lower limit K_d (m^3/kg) values of Am, Cm, and Ln (III) for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.1E+01**	**1.1E+01**	**3.7E+01**	**2.1E+01**	**4.6E+01**	**2.1E+01**	**1.3E+01**
10	2.1E+01	2.1E+01	4.2E+01	1.9E+01	4.2E+01	3.3E-01	1.9E+01

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20 THORIUM

Several of the actinides in spent nuclear fuel are tetravalent in groundwater conditions. One of those is thorium, which is solely tetravalent under the conditions relevant to the environment. The groundwater samples taken for analysis from Olkiluoto were from boreholes OLKR11, at depths of 125-126.5m, and OLKR13, at depths of 214-220m and 362-365m. The Th concentrations ranged from $3 \cdot 10^{-11}$ M to $2 \cdot 10^{-9}$ M (Jernström et al. 2002).

20.1 Speciation

In the glacial meltwater OLGA at pH 5.8, the main species are the hydroxo complexes $Th(OH)_3^+$ and $Th(OH)_4$ (Figure Th-1). The contribution of hydroxocarbonato complexes increases with pH but is minor. At higher pH, $Th(OH)_4$ is the only major species.

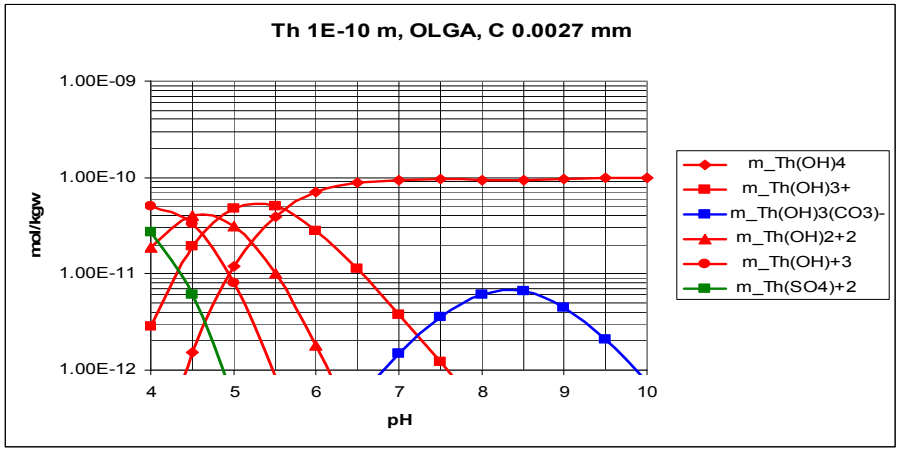

Figure Th-1. *Speciation of Th ($1 \cdot 10^{-10}$ mol/kgw) in glacial meltwater OLGA.*

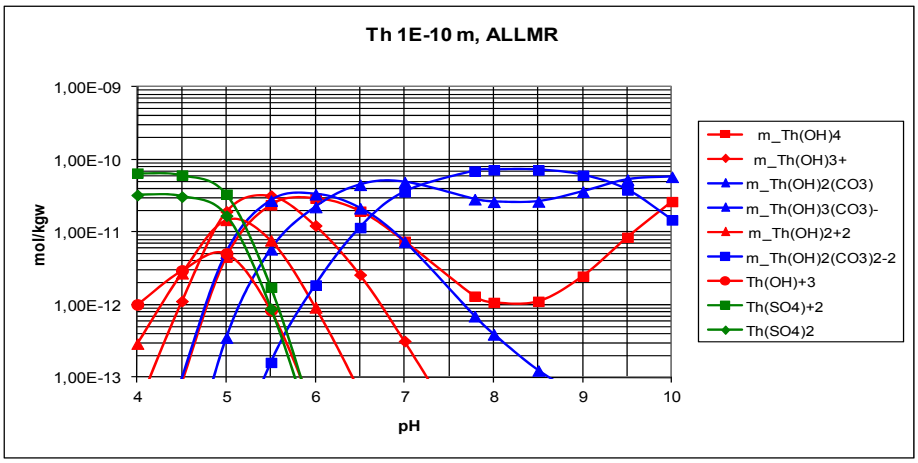

Figure Th-2. *Speciation of Th ($1 \cdot 10^{-10}$ mol/kgw) in fresh reference water ALLMR.*

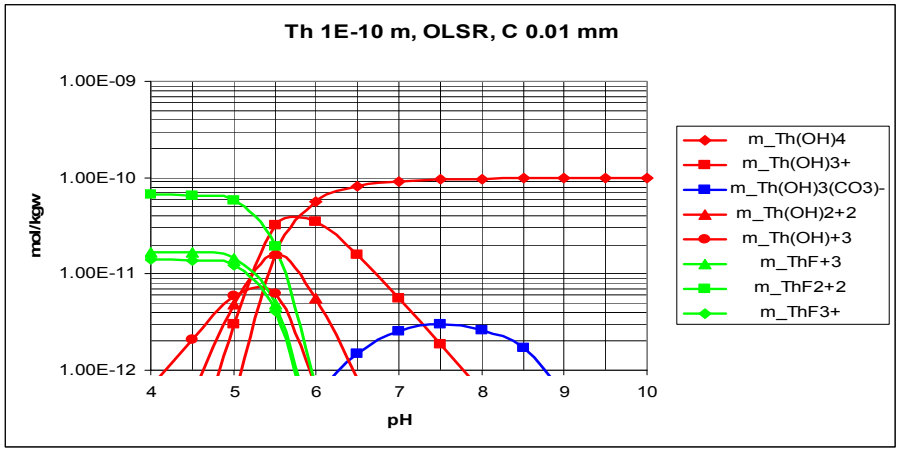

Figure Th-3. *Speciation of Th ($1 \cdot 10^{-10}$ mol/kgw) in saline reference water OLSR.*

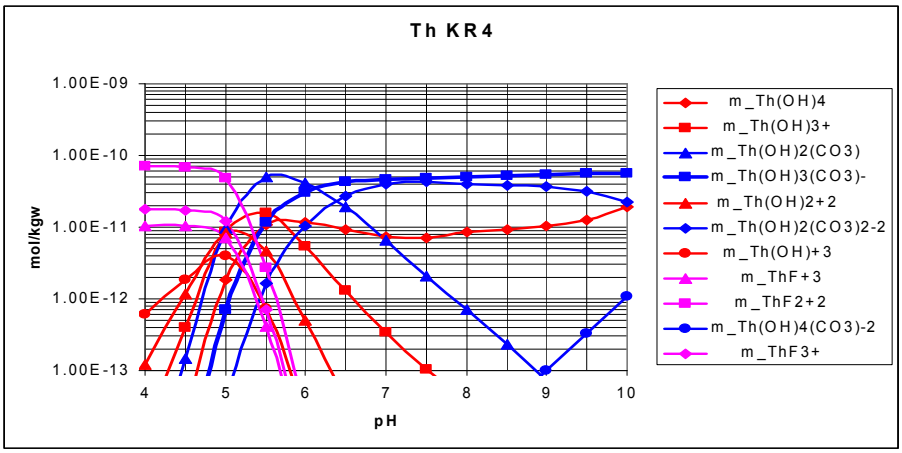

Figure Th-4. *Speciation of Th ($1 \cdot 10^{-10}$ mol/kgw) in KR4_81_1 groundwater.*

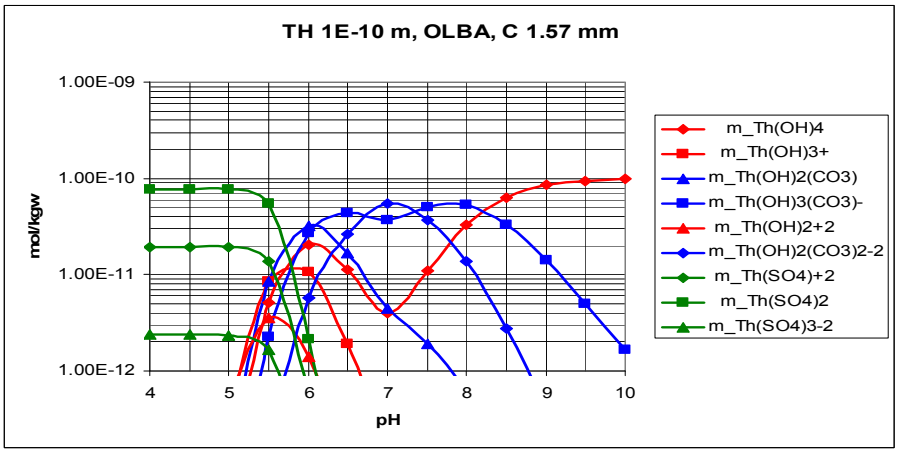

Figure Th-5. *Speciation of Th ($1 \cdot 10^{-10}$ mol/kgw) in brackish reference water OLBA.*

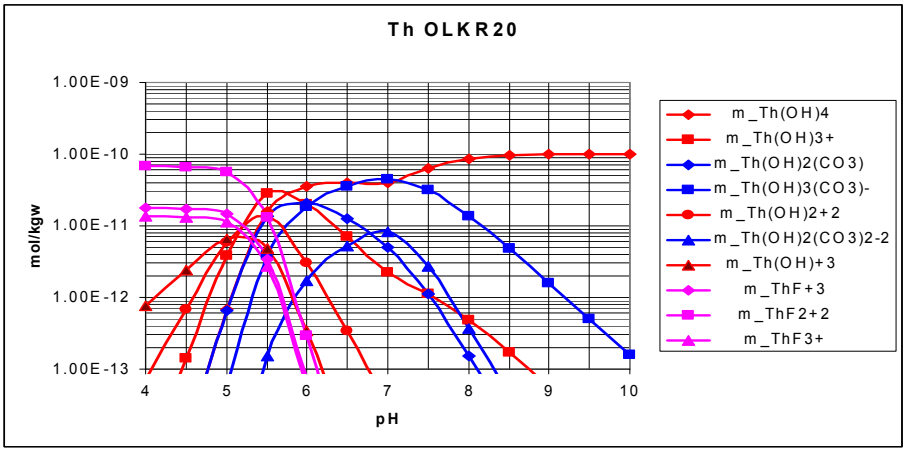

***Figure Th-6**. Speciation of Th ($1 \cdot 10^{-10}$mol/kgw) in KR20_465_1 groundwater.*

The high tendency of Th to form hydroxocarbonato complexes is seen in speciation in the fresh reference water ALLMR. In the calculations, calcite was allowed to precipitate when oversaturated at higher pH. In these calculations, the Th-hydroxosilicato complexes (Rai et al. 2008) were included and the solution was assumed to be in equilibrium with SiO_2(am) to see the maximum impact of dissolved silica. The speciation calculation where excess silicate was not included indicates that the $Th(OH)_4$ is also the main species in ALLMR (Figure Th-2).

The speciation in saline low-carbonate reference water OLSR (Figure Th-3) differs only at low pH from speciation in OLGA. In the saline water, the fluoride complexes are abundant, but only at pH less than 6.

Speciation of Th in brackish KR4_81_1 groundwater (Figure Th-4) is much the same as in brackish reference water OLBA (Figure Th-5). The higher carbonate concentration in KR4_81_1 is followed by an even higher proportion of the Th-hydroxocarbonato complexes. In saline KR20_465_1 groundwater, the $Th(OH)_4$ and Th-hydroxocarbonato complexes are the major species at the nominal pH of this water. At high pH, the low carbonate ion concentrations are followed by the $Th(OH)_4$ complex being the main species.

20.2 Sorption on rocks

20.2.1 Source data

Sorption on quartz

The pH and carbonate concentration dependency of the sorption of Th was determined for non-porous fine ground alpha-quartz Min-U-Sil 5 (U.S. Silica Company) in 0.1 M NaCl under a CO_2-free N_2-atmosphere using Th-234 isotope tracer (Methodology described in Appendix 4). The Th concentration was adjusted to $1 \cdot 10^{-10}$ M and $1 \cdot 10^{-8}$ M by the addition of Th-232 to the solution. The total carbonate concentration was adjusted to 0.2mmol/kgw and 2 mmol/kgw by Na-bicarbonate. Speciation calculation

indicates that at neutral pH the $Th(OH)_4$ and the Th hydroxo complexes are the main species, the proportion of $Th(OH)_4$ increasing with the increase of total carbonate in the solution. For 2 mmol/kgw total carbonate concentration the hydroxocarbonato complexes are the main species at pH higher than 5.5 (Figure Th-7).

The R_d values were at a maximum at neutral pH and also decreased with the increasing pH in the carbonate free solution (Figure Th-8). Increase of carbonate concentration from 0.2 to 2 mmol/L was followed by a decrease in R_d values (Figure Th-9). The decrease of sorption on the Min-U-Sil quartz with increase of pH at a pH higher than 7 may be due to Th hydroxocarbonato complexation, and at high pH due to hydroxosilicato complexation, as suggested by the large impact of this complex when solution was taken to be in equilibrium with amorphous silica. In the speciation calculation, the proportion of $Th(OH)_4$ at pH 10 is about the same in all solutions. This is in agreement with the finding that the R_d values at pH 10 are not very different.

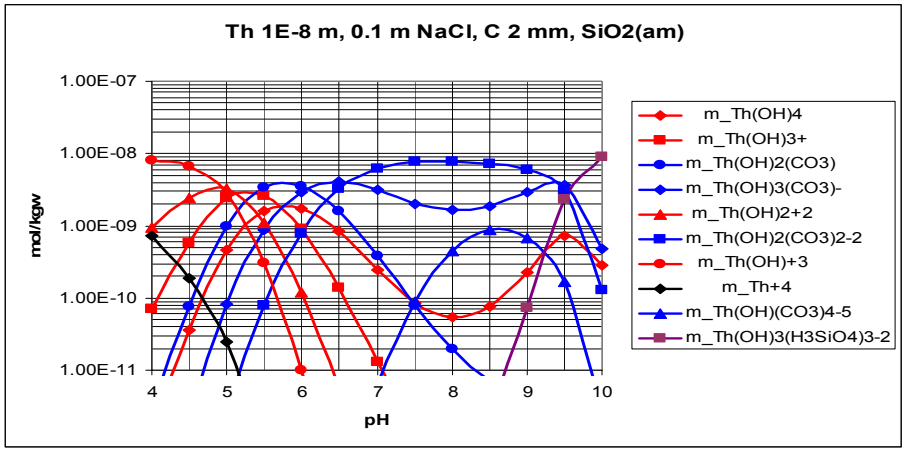

Figure Th-7. *Speciation of Th ($1 \cdot 10^{-8}$mol/kgw) in 0.1 M NaCl solution. In total carbonate concentration 2 mmol/kgw in the presence of amorphous silica.*

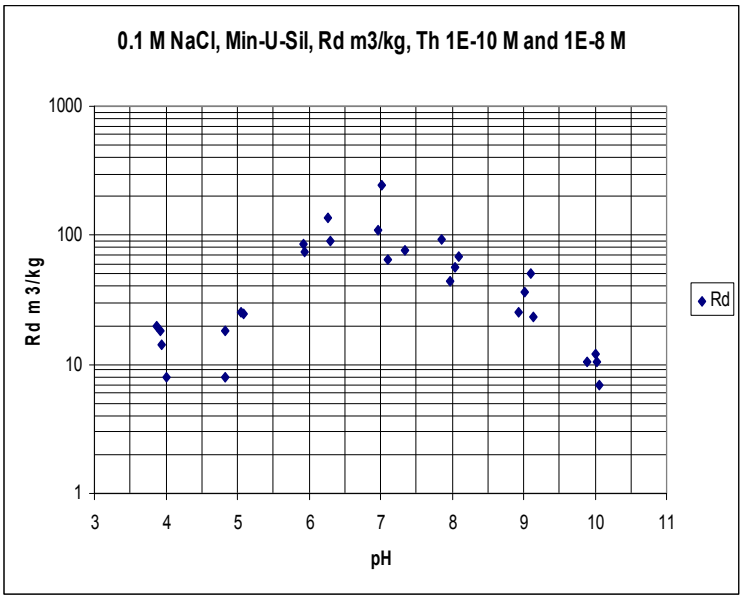

Figure Th-8. *R_d values (m^3/kg) of Th for Min-U-Sil quartz in carbonate-free 0.1 M NaCl.*

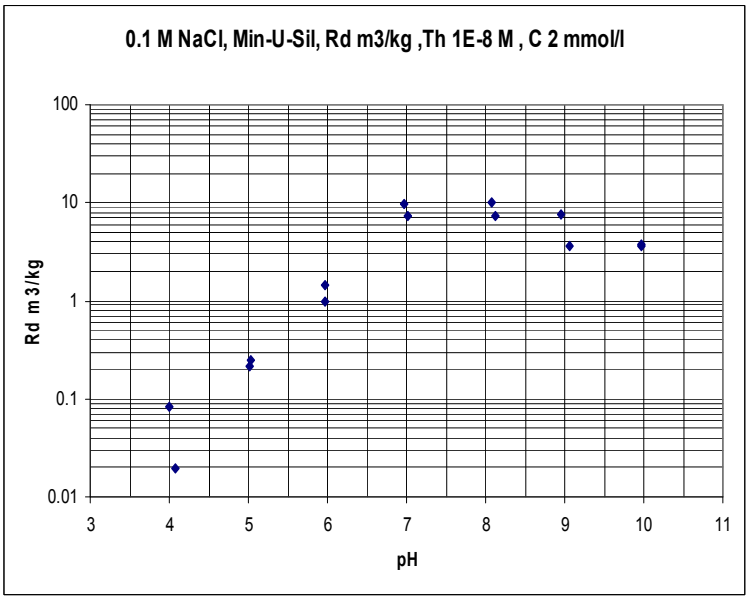

Figure Th-9. *R_d (m^3/kg) of Th for Min-U-Sil quartz in 0.1 M NaCl with 2 mmol/l total carbonate concentration.*

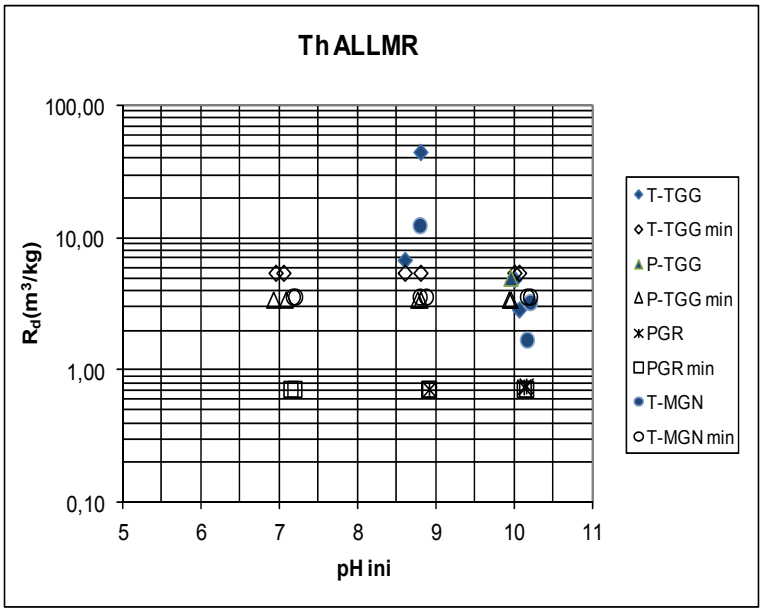

Figure Th-10. *K_d values (m^3/kg) of Th for the rocks in ALLMR reference water. The values corresponding to LLD (2σ) count rate are indicated with open symbols (min).*

Sorption on reference rocks

The R_d values of Th on the crushed reference rocks were determined in ALLMR type water having total carbonate concentration 1.1 mM and in saline reference water OLSR, using Th-234 isotope tracer (Methodology described in Appendix 4). The experiments were carried out under a carbonate-free N_2 atmosphere. The solid to solution ratio was 1:10.

The crushed rocks were relatively coarse grained. One gramme of the rock batch was used in the sorption experiments to ensure the homogeneity of the sub-samples. The maximum volume that could be taken to radioactivity counting on the LSC counter is 20 mL. In the experiments, the count rate in solution at the end of experiment was in many samples lower than the LLD for 2 σ sigma statistics. The K_d values indicated by open symbols in Figures Th-10 and Th-11 are derived from the R_d values corresponding to LLD.

20.2.2 Best estimate K_d values

As suggested by the results for the clays, the (modelled) hydroxocarbonato complexation of Th in the groundwaters does not reduce sorption compared with sorption in low-carbonate conditions.

Due to scattering of the K_d values derived from sorption experiments, the K_d values for the T-series mica gneiss T-MGN in Figures Th-10 and Th-11 and K_d values of Sn (IV) and Pu(IV) are compared in Table Th-1. The LFER (Linear Free Energy Relationship) theory suggests that the order of sorption of tetrahydroxo complexes should be Th<Pu(IV)<Sn. The main species of Sn is $Sn(OH)_4$ and of Pu is $Pu(OH)_4$. The order

between the K_d values in Table Th-1 is in agreement with the LFER theory. Bradbury & Baeyens (2005) give K_d values for Sn and Th in the inert electrolyte under CO_2-free conditions for montmorillonite. Their K_d value for Th at pH 7-8 is about half of the value of Sn.

The K_d values in saline reference water OLSR (Figure Th-11) are less scattered than values for fresh ALLMR reference water and include more values that are not lower limit values. In the selection of the best estimate value, more weight is given to the values in OLSR. Sorption on clays in the waters in this report shows no direct dependence of R_d values on the hydroxocarbonato complexation of Th. The mean of K_d values for ALLMR and OLSR for T-MGN Olkiluoto T-series mica gneiss is 8 m^3/kg. This is suggested to be the best estimate value for T-MGN in the waters at pH higher than 7. At pH 6, the K_d values for kaolinite in the waters were about one third of the value at pH 7-8. This ratio is used for K_d values for the rocks in OLGA and other waters. The best estimate values are shown in Tables Th-2 – Th-5. See Figure Th-12, which shows the R_d values (m^3/kg) of Th on HKGa-1b kaolinite in 0.1 M NaCl with 2 mM total carbonate.

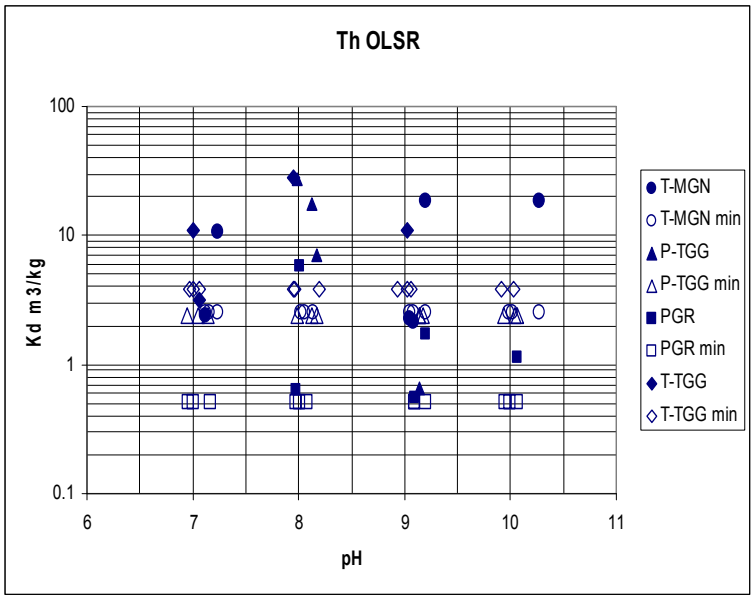

Figure Th-11. *K_d values (m^3/kg) of Th for the rocks in OLSR saline reference water. The values corresponding to LLD (2σ) count rate are indicated with open symbols (min). Rocks: T-MGN=T-series mica gneiss, P-TGG=P-series tonalite granodiorite granite gneiss, T-TGG=T-series tonalite granodiorite granite gneiss, PGR= pegmatitic granite.*

Table Th-1. *K_d values (m^3/kg) of thorium for T-MGN T-series mica gneiss in Figures Th-10, Th-11 and K_d values for Sn and Pu at pH 7-8.*

Water/pH	Th	Sn	Pu
ALLMR/7-8	4	16	12
OLSR/7-8	10		
Best estimate	8		

Table Th-2. *Best estimate K_d values (m^3/kg) of thorium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**
10	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00

Table Th-3. *Best estimate K_d values (m^3/kg) of thorium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Th-4. *Best estimate K_d values (m^3/kg) of thorium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Th-5. *Best estimate K_d values (m^3/kg) of thorium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-01**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**
10	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00

20.2.3 Lower limit K_d values

The uncertainty in the K_d values for the rocks originates from the scatter of the measured R_d values and from the mineralogical uncertainties. In addition to the mineralogical uncertainties, the scatter in the K_d values in Figures Th-10 and Th-11 must be taken into account in the total uncertainty. The uncertainty factors are chosen so that all of the values in Figures Th-10 and Th-11 are covered (Table Th-6). The lower values for T-MGN, P-TGG, T-TGG and PGR are calculated by dividing the best estimate K_d value by the corresponding uncertainty factor. The lower limit K_d values are given in Tables Th-7 – Th-10.

Table Th-6. *The uncertainty factors of thorium for rocks. T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

Reference rock	Factor for random error calculation
T-MGN, P-TGG	20
T-TGG	20*
PGR	50*
*error propagation using the errors in the mica contents and BET (surface area) of micas and crushed rock yield unrealistically high correction factor for T-MGN and PGR. Omitting the error in BET of crushed rock, the factor for T-TGG is 7 and for PGR 43.	

Table Th-7. *Lower limit K_d values (m^3/kg) of thorium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**
10	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01

Table Th-8. *Lower limit K_d values (m^3/kg) of thorium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-02**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Th-9. *Lower limit K_d values (m^3/kg) of thorium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E-02**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Th-10. *Lower limit K_d values (m^3/kg) of thorium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**
10	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02

20.3 Sorption on clays

20.3.1 Source data

Sorption on clays

Sorption on the clay kaolinite KGa-1b was determined in 0.1M NaCl solution and in the reference waters. Sorption on illite IMt-1 and chlorite CCa-2 was determined in the reference waters. The pH was varied by the addition of HCl and NaOH.

Kaolinite

Sorption of Th ($1 \cdot 10^{-11}$ M) on kaolinite HKGa-1b was determined in 0.1 M NaCl with 2 mM total carbonate. The R_d values in Figure Th-12 indicate a decrease of sorption with increasing pH on kaolinite HKGa-1b (Methodology described in Appendix 4).

Sorption in the reference waters on kaolinite KGa-1b was determined using Th-concentration $1 \cdot 10^{-10}$ M. No pH buffers were used. This was followed by changes of pH from the initial level being found. The final pH values in the reference waters OLGA, ALLMR and OLBA were about one pH unit higher than the initial values. Figure Th-13 indicates the R_d values for the initial pH.

Illite

The Th concentration used in the sorption experiments on illite IMt-1 was $1 \cdot 10^{-10}$ M. No pH buffers were used. Figure Th-14 indicates the sorption of Th as a function of initial pH. Speciations of Th in the waters do not support lower sorption in the low ionic strength waters ALLMR and OLGA at high pH. The low R_d value may be due to the

formation of colloidal particles that were not separated from the solution taken for radioassay. The values at pH 10 in ALLMR and OLGA are omitted in the estimation of the K_d values.

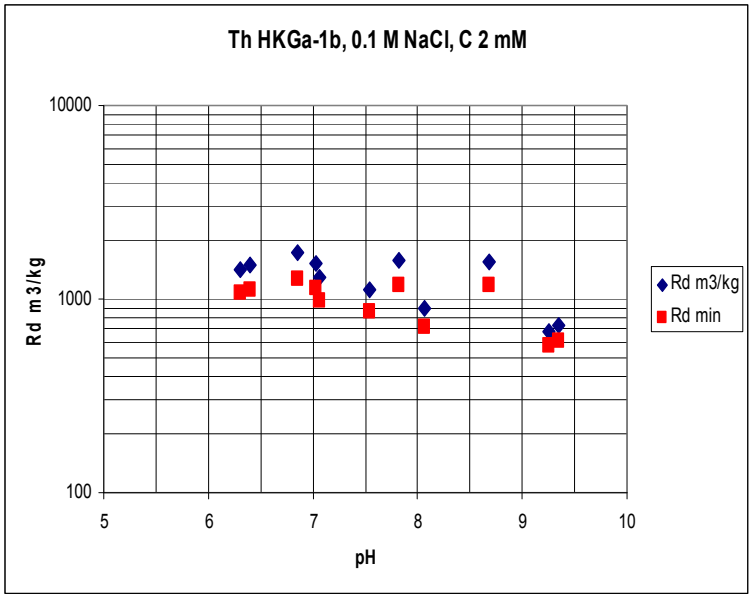

Figure Th-12. *R_d values (m^3/kg) of Th on HKGa-1b kaolinite in 0.1 M NaCl with 2 mM total carbonate. Red squares indicate lower limit (2σ) values (min).*

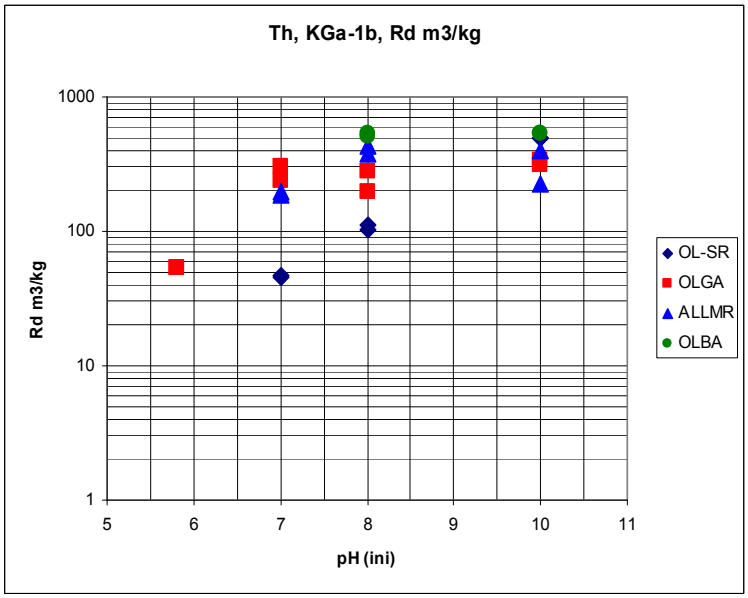

Figure Th-13. *R_d values (m^3/kg) of Th for KGa-1b kaolinite in the reference waters. The initial pH values of the solutions are given.*

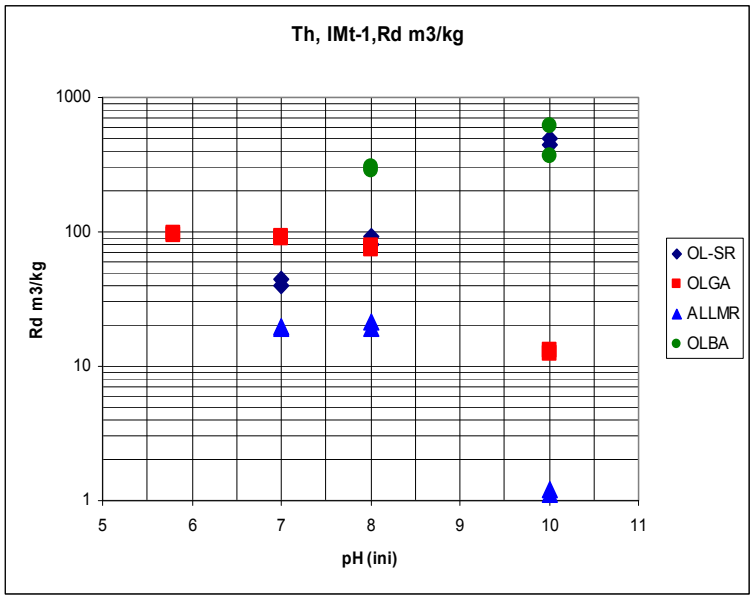

Figure Th-14. *R_d values (m^3/kg) of Th for illite in the reference waters. The initial pH values of the solutions are given.*

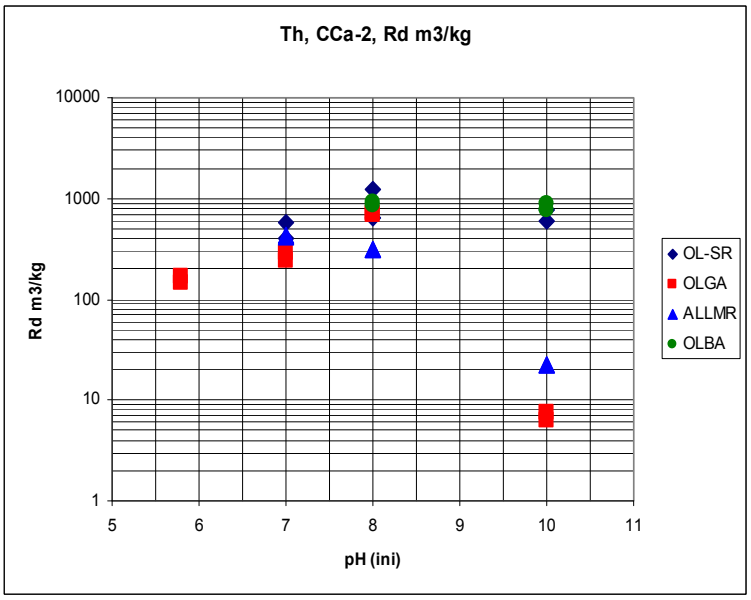

Figure Th-15. *R_d values (m^3/kg) of Th for CCa-2 chlorite in the reference waters. The initial pH values of the solutions are given.*

Chlorite (ripidolite)

The Th concentration used in the sorption experiments on chlorite (ripidolite CCa-2) was $1 \cdot 10^{-10}$ M. No pH buffers were used. Figure Th-15 indicates the sorption of Th as a function of initial pH. Speciation in the low ionic strength reference waters ALLMR and

OLGA does not support the low sorption at pH 10 and the points are omitted in the estimation of the K_d values.

20.3.2 Best estimate K_d values

The speciation of Th in the reference waters OLBA and ALLMR indicates that in these waters the Th-hydroxocarbonato complexes are the main species at pH 7-8 and 7-9 respectively and the proportion of $Th(OH)_4$ is 5-10% and 1-2%. The differences in the calculated speciations are not seen in the sorption on the clays in the reference waters, even when sorption on quartz in NaCl was obviously reduced.

The LFER (Linear Free Energy Relationship) theory suggests that sorption of Th in carbonate-free inert electrolyte solution, best presented by OLGA and OLSR waters in this report, is lower than the sorption of Sn(IV), Pu(IV) and Np (IV). Compared with the sorption of Sn in this report, the sorption of Th is lower, in agreement with the LFER relationship.

At pH 6, the sorption on the kaolinite KGa-1b and the chlorite CCa-2 in the reference water OLGA is lower than at pH 7-8. This trend is the same as in the changes of the proportion of $Th(OH)_4$ of total Th.

Table Th-11. *Best estimate K_d values (m^3/kg) of thorium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E+01**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**
10	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02

Table Th-12. *Best estimate K_d values (m^3/kg) of thorium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**
10	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01

Table Th-13. *Best estimate K_d values (m^3/kg) of thorium for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

	Chlorite					
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+02**	**3.0E+02**	**3.0E+02**	**3.0E+02**	**3.0E+02**	**3.0E+02**
10	3.0E+02	3.0E+02	3.0E+02	3.0E+02	3.0E+02	3.0E+02

At high pH, the R_d values for the clays are scattered. Results for kaolinite KGa-1b (Figure Th-13) suggest no reduction in sorption. For the illite IMt-1 and the chlorite CCa-2 in low-ionic strength waters at pH 10, the measured R_d values are low, most probably due to experimental difficulties. Speciations in the waters do not support the reduction in R_d values at high pH.

The R_d values for the kaolinite KGa-1b in the reference waters are lower than in 0.1 M NaCl. The results in the reference water are preferred to be used as the best estimate K_d values. The best estimate K_d values are given in Tables Th-11 – Th-13.

20.3.3 Lower limit K_d values

The overall uncertainty factor (UF) for intact fracture clays at Olkiluoto is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source}*UF_{model}*UF_{CEC}*UF_{spec}*UF_{pH}*UF_{lab\_field} \quad \text{(Th-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\ (LL) = K_d(BE)/UF_{tot} \quad \text{(Th-2)}$$

Kaolinite

UF_{source} varies from 1.1 to 1.2. Owing to the high sorption of Th, there was scatter in the measured R_d values. This brings uncertainty, which was taken into account when choosing the lowest R_d values for the calculations of best estimate K_d values. One sigma deviation in R_d values at the lowest R_d value is included in the uncertainty factor.

UF_{CEC} = 1. The sorption mechanism is ion exchange. At higher pH, the impact of sorption by surface complexation is not taken into account. Since the source data were performed in well-crystallised kaolinite, there is no need for a correction factor concerning differences between the source data and reference conditions. Well-crystallised kaolinite sorbs in equal amounts or less compared with the Olkiluoto kaolinite (the state of crystallinity is unknown). However, the CEC for kaolinite is in general not very high, and it was considered that the uncertainty is not significant (see Chapter 3).

UF_{spec} varies from 1 to 1.4. When no difference in speciation is expected between the groundwater and reference water from which the best estimate K_d values of groundwater were calculated, the uncertainty factor UF_{spec} is taken as 1. Otherwise it is taken as 1.4.

UF_{pH} = 1. There is no pH dependency on K_d values and the source data are used without pH calculation.

UF_{lab_field} = 2. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 2.7 to 3.8.

The uncertainty factors are collected in Table Th-14. Only those factors which are greater than one are listed. The lower limit K_d values for kaolinite at Olkiluoto are calculated in Table Th-17.

Illite

$UF_{source} = 1$.

$UF_{CEC} = 1.3$. The uncertainty in the source material compared with the Olkiluoto site illite is taken into account in the uncertainty factor UF_{CEC}, since the CEC of the source data illite and the Olkiluoto illite may be significantly different.

UF_{spec} varies from 1 to 1.4. When no difference in speciation is expected between the groundwater and reference water from which the best estimate K_d values of groundwater were calculated, the uncertainty factor UF_{spec} is taken to be 1. Otherwise it is taken to be 1.4.

$UF_{lab\_field} = 2$. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 2.7 to 3.8.

The uncertainty factors are collected in Table Th-15. Only those factors which are greater than one are listed. The lower limit K_d values for illite at Olkiluoto are calculated in Table Th-18.

Chlorite

UF_{source} varies from 1.1 to 1.2. Owing to the high sorption of Th, there was scatter in the measured R_d values. This brings uncertainty, which was taken into account when choosing the lowest R_d values for the calculations of best estimate K_d values. One sigma deviation in R_d values at the lowest R_d value is included in the uncertainty factor.

$UF_{CEC} = 1.3$. The uncertainty in the source material compared with the Olkiluoto site chlorite is taken into account in the uncertainty factor UF_{CEC}, since the CEC of the source data chlorite and the Olkiluoto chlorite may be significantly different.

UF_{spec} varies from 1 to 1.4. When no difference in speciation is expected between the groundwater and the reference water from which the best estimate K_d values of groundwater were calculated, the uncertainty factor UF_{spec} is taken to be 1. Otherwise it is taken to be 1.4.

$UF_{lab\_field} = 2$. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 3 to 4.3.

The uncertainty factors are collected in Table Th-16. Only those factors which are greater than one are listed. The lower limit K_d values for chlorite at Olkiluoto are calculated in Table Th-19.

Table Th-14. *The uncertainty factors (UF) of Th for kaolinite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{spec}	UF_{Lab_field}	UF_{tot}
OLGA	5.8	1.1	1	2	2.2
	10	1.2	1	2	2.4
ALLMR	-	1.2	1	2	2.4
OLBA	-	1.2	1	2	2.4
OLSR	-	1.2	1	2	2.4
KR4	-	1.2	1.4	2	3.3
KR20	-	1.2	1.4	2	3.3

Table Th-15. *The uncertainty factors (UF) of Th for illite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	UF_{source}	UF_{cec}	UF_{spec}	UF_{Lab_field}	UF_{tot}
OLGA	1	1.3	1	2	2.7
ALLMR	1	1.3	1	2	2.7
OLBA	1	1.3	1	2	2.7
OLSR	1	1.3	1	2	2.7
KR4	1	1.3	1.4	2	3.8
KR20	1	1.3	1.4	2	3.8

Table Th-16. *The uncertainty factors (UF) of Th for chlorite at Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	pH	UF_{source}	UF_{cec}	UF_{spec}	UF_{Lab_field}	UF_{tot}
OLGA	5.8	1.1	1.3	1	2	2.9
	10	1.2	1.3	1	2	3
ALLMR	-	1.2	1.3	1	2	3
OLBA	-	1.2	1.3	1	2	3
OLSR	-	1.2	1.3	1	2	3
KR4	-	1.2	1.3	1.4	2	4.3
KR20	-	1.2	1.3	1.4	2	4.3

Table Th-17. *Lower limit K_d (m^3/kg) values of Th for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E+01**	**8.4E+01**	**8.3E+01**	**8.4E+01**	**6.0E+01**	**6.0E+01**
10	8.4E+01	8.4E+01	8.4E+01	8.4E+01	6.0E+01	6.0E+01

Table Th-18. *Lower limit K_d (m^3/kg) values of Th for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E+00**	**7.5E+00**	**7.5E+00**	**7.5E+00**	**5.3E+00**	**5.3E+00**
10	7.5E+00	7.5E+00	7.5E+00	7.5E+00	5.3E+00	5.3E+00

Table Th-19. *Lower limit K_d (m^3/kg) values of Th for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Chlorite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.5E+01**	**9.9E+01**	**9.9E+01**	**9.9E+01**	**7.0E+01**	**7.0E+01**
10	9.9E+01	9.9E+01	9.9E+01	9.9E+01	7.0E+01	7.0E+01

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Jernström, J., Vuorinen, U., Hakanen, M. 2002. Solubility of thorium in 0.1 M NaCl solution and in saline and fresh anoxic reference groundwater. Posiva Oy, Olkiluoto, Finland, Posiva Report 2002-06.

Rai, D., Yui, M., Moore, D.A., Lumetta, G.J., Rosso, K.M., Xia, Y., Felmy, A.R., Skomurski, F.N. 2008. Thermodynamic Model for ThO_2(am) Solubility in Alkaline Silica Solutions. J. Solution Chem. 37, 1725–1746.

21 PROTACTINIUM

21.1 Speciation

Very little is known about the complexation chemistry of Pa in groundwaters. Tarapcik et al. (2005) have estimated the E^0 to be -0.1 V for the reduction of Pa (V) to Pa (IV). Pa(V) is assumed to be the oxidation state in bedrock conditions. According to the present knowledge, the chemistry is dominated by the hydrolysis reactions of Pa(V). Speciation using the data in Baes & Mesmer (1986) suggest that Pa(V) is in solution from pH 6 to pH 10 in the form of $PaO_2(OH)$. Under reducing conditions, the hydrolysis data selected by Duro et al. (2006) gives the dominating species as $PaO(OH)^+$ ($PaO2^+$) for the pH range 6 to 10 (Figure Pa-1). More recent studies on the hydrolysis of Pa(V) have been published by Trubert et al. (2002) and Le Naour et al. (2003) and complemented by Fourest et al. (2004). Fourest et al. measured the diffusion of Pa(V) in capillary experiments and suggested that in basic aerobic conditions, in addition to cationic and neutral hydroxo complexes, an anionic Pa(V) hydroxo complex is formed, probably $PaO_2(OH)_2^-$ (Fourest et al. 2004). It follows also that the solubility of Pa increases with pH. In their modelling results, the proportion of this anionic complex increases from 5 % at pH 8 to 90 % at pH 10. Speciation of Pa(V) in OLSR was calculated using the data base of Duro et al. (2006) (Figure Pa-1) and Thermo_Chimie Version 7b (ANDRA 2009), which includes data from Fourest et al. (2004) (Figure Pa-2). The species $PaO(OH)^{2+}$ was included in the calculations. Its impact is smaller than 0.1 % at pH 5 and higher. Sulphate complexation in the reference waters was also included in the calculations using formation constants in Di Giandomenico & Le Naour (2009), and its impact on speciation was found to be minor in OLSR water. The speciation using Thermo_Chimie TDB suggests the formation of an anionic hydroxo complex, the proportion of which increases with pH from 1% at pH 7.5 to 90 % at pH 10.

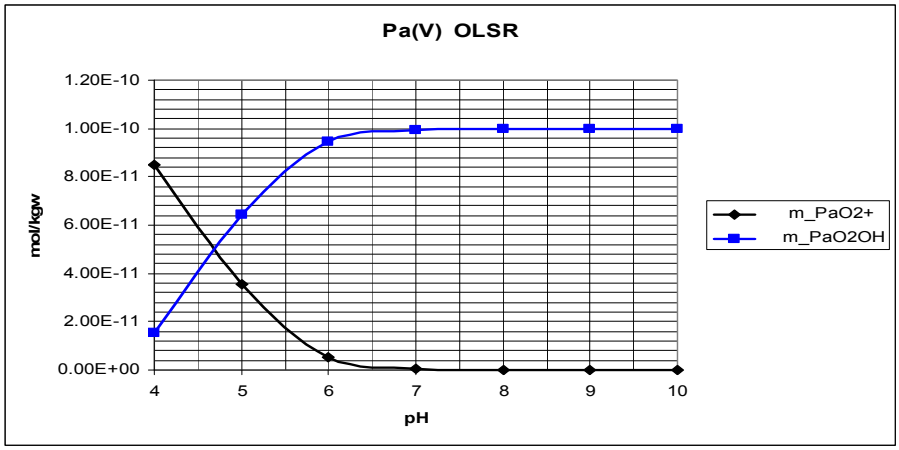

Figure Pa-1. *Speciation of Pa (V) in saline reference water OLSR using the data in Duro et al. (2006).*

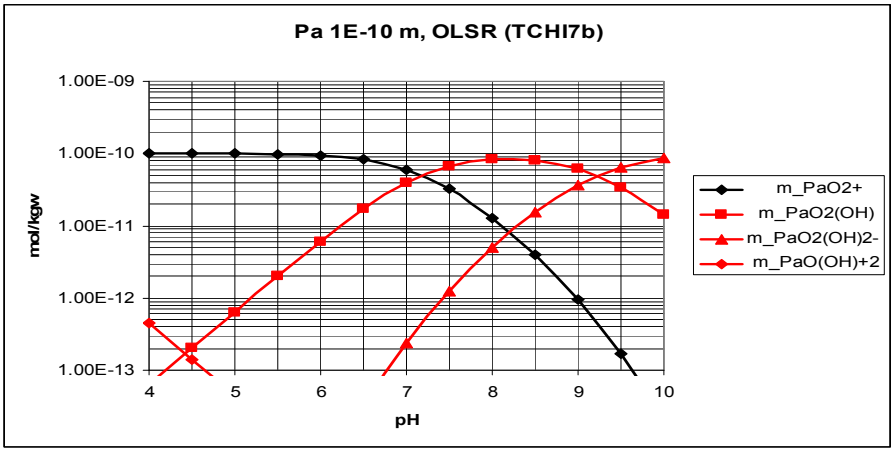

Figure Pa-2. *Speciation of Pa (V) in saline reference water OLSR using Thermo Chimie vers. 7b TDB.*

21.2 Sorption on rocks

Sorption of Pa on Olkiluoto mica gneiss, tonalite and granite in OLKR5 water has been determined by Kulmala et al. (1996). The work also included rocks and waters from Romuvaara and Kivetty. Sorption on crushed rapakivi granite in brackish groundwater was determined in Huitti et al. (1996).

Sorption of actinides Pa(V) on Na-illite in 0.1 M $NaClO_4$ at pH 2 to pH 11 has been determined and modelled by Bradbury & Baeyens (2009). The R_d values of Pa(V) ranged from 40 m^3/kg at pH 6–7 to 100 m^3/kg at pH 9–10. The R_d values were lower than for Th on the illite.

21.2.1 Source data

Sorption on rocks in Olkiluoto OLKR5 groundwater

Sorption of Pa on Olkiluoto mica gneiss, tonalite and granite in saline OLKR5 water was determined in aerobic and anaerobic conditions by Kulmala et al. (1996). The Pa-233 tracer isotope was separated from Np-237, and the Pa-231 isotope was used as a carrier. The concentration of Pa was $6.6 \cdot 10^{-13}$ M and $2.9 \cdot 10^{-10}$ M. The R_d values of mica gneiss under aerobic conditions were 1.3 – 3.1 m^3/kg and 0.8 – 1.1 m^3/kg (pH 8.0–8.3) under anaerobic conditions. No difference in R_d values for the two initial Pa concentrations was detected. For the other rocks, the R_d values under aerobic conditions were 0.7 – 1.2 m^3/kg and 1.0 – 2.4 m^3/kg.

Sorption in reference groundwaters

The sorption of protactinium (Pa-233 separated from Np-237 solution) was studied on two rocks, P-series granodiorite gneiss (P-TGG) and pegmatite granite (PGR). The waters were fresh ALLMR and saline OLSR. The batch experiments were performed under an argon atmosphere (Appendix 4). The Pa-233 concentration was about $1 \cdot 10^{-13}$ M. The R_d values of Pa on the rocks P-TGG and PGR are presented in Figures Pa-3 and Pa-4.

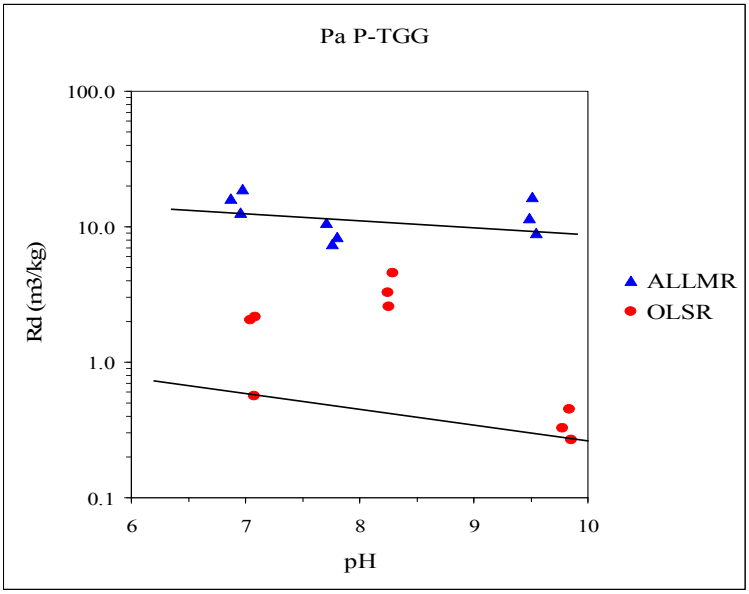

Figure Pa-3. *R_d values of Pa on rock P-TGG in fresh ALLMR and saline OLSR water.*

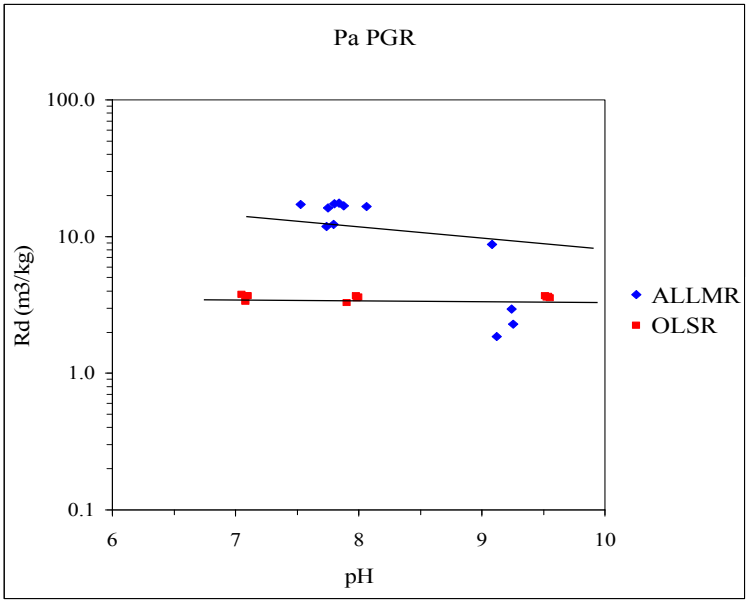

Figure Pa-4. *R_d values of Pa on rock PGR in fresh ALLMR and saline OLSR water.*

21.2.2 Best estimate K_d values

The best estimate K_d values were calculated from the R_d data for the reference rocks in the fresh and saline groundwater simulants. The R_d values of P-TGG in ALLMR water and of PGR in OLSR water are, within the scatter of values, the same for pH range 6 – 10 as the Rd values for illite in 0.1 M $NaClO_4$ (Bradbury and Baeyens 2009). For P-TGG in OLSR and PGR in ALLMR also, R_d values nearly one order of magnitude lower than the highest values were determined. The conservative approach was adopted

for the derivation of the best estimate values. The procedure is backed up by the results in Kulmala et al. (1996) and Huitti et al. (1996), and R_d values in JNC-SDB for granodiorite.

K_d values of protactinium were derived from the R_d values with the following method. Owing to the scatter of R_d values in OLSR to P-TGG and in ALLMR to PGR, a straight line was drawn to a level such that most of the R_d values lay above the line. The R_d values for a pH were derived with the help of the line. The factors for converting the R_d values for the crushed rocks to K_d values of intact rock are given in Chapter 3. The K_d values for T-MGN and T-TGG were derived from the R_d values for P-TTG using the ratio of mica contents as the scaling factor and converting the R_d values to K_d values using the ratio of R_d to K_d conversion factor for the rocks. The difference between the R_d values in ALLMR and OLSR waters seen in Figures Pa-3 and Pa-4 are not supported by speciation of Pa in solution. The R_d values in OLSR for P-TGG are smaller than those for PGR. So as not to overestimate sorption, the values of P-TGG were used in the derivation of the K_d values in OLSR. The values of OLGA and OLGO waters were calculated from the values of ALLMR. The values of OLBA and OLSO were calculated from the values of OLSR. The best estimate K_d values of protactinium for T-MGN, P-TGG, T-TGG and PGR rocks are presented in Tables Pa-1– Pa-4.

The K_d values derived from R_d data for P-TGG in ALLMR to T-MGN are in fair agreement with the K_d values derived for T-MGN from R_d data of Pa in OLKR5 water. The new best estimate values in saline waters are lower than those derived from data in Kulmala et al. (1996).

Table Pa-1. *The best estimate K_d (m^3/kg) values of protactinium for mica gneiss T-MGN at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81;_1 KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E+00**	**2.7E+00**	**2.2E+00**	**1.1E-01**	**1.0E-01**	**1.1E-01**	**1.1E-01**
10	1.8E+00	1.8E+00	1.8E+00	6.0E-02	6.0E-02	6.0E-02	6.0E-02

Table Pa-2. *The best estimate K_d (m^3/kg) values of protactinium for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.4E+00**	**1.4E+00**	**1.1E+00**	**6.0E-02**	**5.0E-02**	**6.0E-02**	**6.0E-02**
10	9.0E-01	9.0E-01	9.0E-01	3.0E-02	3.0E-02	3.0E-02	3.0E-02

Table Pa-3. *The best estimate K_d (m^3/kg) values of protactinium for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.2E+00**	**1.2E+00**	**1.0E+00**	**5.1E-02**	**4.3E-02**	**5.1E-02**	**4.3E-02**
10	8.4E-01	8.4E-01	8.4E-01	2.5E-02	2.5E-02	2.5E-02	2.5E-02

Table Pa-4. *The best estimate K_d (m^3/kg) values of protactinium for pegmatitic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.2E-01**	**6.2E-01**	**4.4E-01**	**1.7E-02**	**1.7E-02**	**1.7E-02**	**1.7E-02**
10	3.1E-01	3.1E-01	3.1E-01	1.7E-02	1.7E-02	1.7E-02	1.7E-02

21.2.3 Lower limit K_d values

The uncertainty factor covers both the mineralogical and chemical uncertainties in solutions. The lower limit K_d value is calculated by dividing the best estimate value by the uncertainty factor. The factors for the Olkiluoto rocks are presented in Table Pa-5. The lower limit K_d values of Pa for the Olkiluoto rocks in reference waters are presented in Tables Pa-6 – Pa-9.

Table Pa-5. *Uncertainty factors for the lower limit K_d values of the Olkiluoto rocks.*

Rock	Uncertainty factor
T-MGN	5
P-TGG	5
T-TGG	20
PGR	50

Table Pa-6. *The lower limit K_d (m^3/kg) values of protactinium for mica gneiss at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.4E-01**	**5.4E-01**	**4.4E-01**	**2.2E-02**	**2.0E-02**	**2.2E-02**	**2.2E-02**
10	3.6E-01	3.6E-01	3.6E-01	1.2E-02	1.2E-02	1.2E-02	1.2E-02

Table Pa-7. *The lower limit K_d (m^3/kg) values of protactinium for P series granodiorite gneiss P-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.8E-01**	**2.8E-01**	**2.2E-01**	**1.2E-02**	**1.0E-02**	**1.2E-02**	**1.2E-02**
10	1.8E-01	1.8E-01	1.8E-01	6.0E-03	6.0E-03	6.0E-03	6.0E-03

Table Pa-8. *The lower limit K_d (m^3/kg) values of protactinium for T series granodiorite gneiss T-TGG at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-02**	**6.0E-02**	**5.0E-02**	**2.6E-03**	**2.2E-03**	**2.6E-03**	**2.2E-03**
10	4.2E-02	4.2E-02	4.2E-02	1.3E-03	1.3E-03	1.3E-03	1.3E-03

Table Pa-9. *The lower limit K_d (m^3/kg) values of protactinium for pegmatic granite PGR at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.2E-02**	**1.2E-02**	**8.8E-03**	**3.4E-04**	**3.4E-04**	**3.4E-04**	**3.4E-04**
10	6.2E-03	6.2E-03	6.2E-03	3.4E-04	3.4E-04	3.4E-04	3.4E-04

21.3 Sorption on clays

21.3.1 Source data

The sorption experiments on protactinium for the clays were performed in fresh granitic groundwater ALLMR and saline groundwater OLSR. The clays were a well-crystallised kaolinite KGa-1b and illite IMt-1 (Clay Mineral Society). The R_d values of Pa on the clays are presented in Figures Pa-5 and Pa-6.

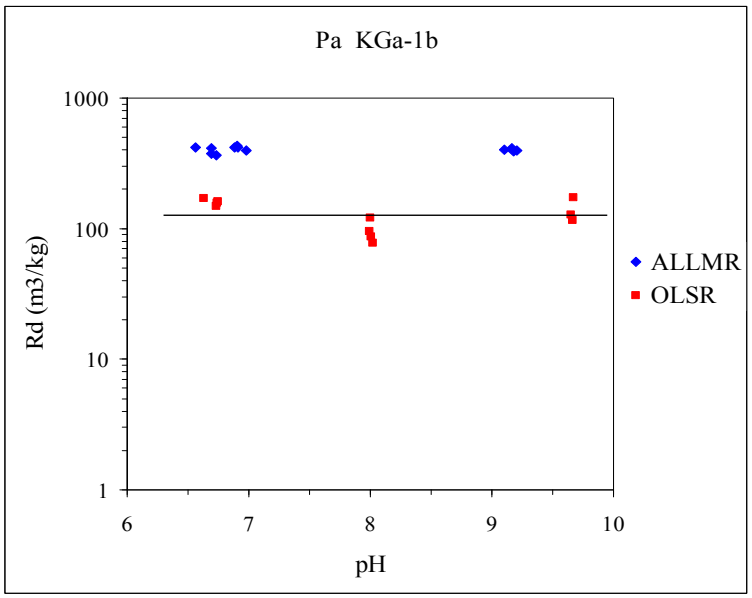

Figure Pa-5. *Sorption of Pa on kaolinite KGa-1b in fresh ALLMR and saline OLSR waters. The R_d values in OLSR are lower limit values.*

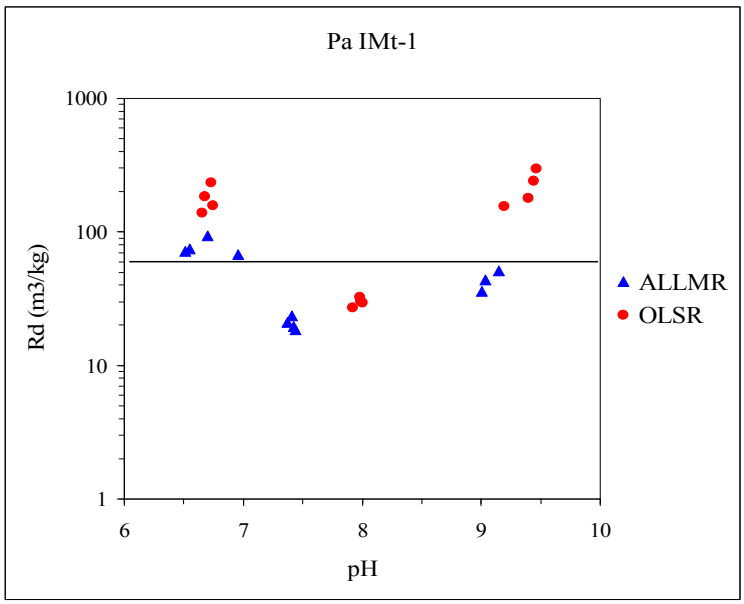

Figure Pa-6. *Sorption of Pa on illite IMt-1 in fresh ALLMR and saline OLSR waters. The R_d values in ALLMR are lower limit values.*

21.3.2 Best estimate K_d values

The R_d values of Pa for kaolinite KGa-1b were high both in the ALLMR and OLSR waters. For many samples, only the detection limit value of R_d could be determined. As a conservative measure, the K_d values were derived from the OLSR R_d results. The

same value was chosen for all waters. As the best estimate values to clays, the K_d values are the same as the R_d values.

In the case of illite IMt-1, there was no explanation as to why the R_d values of OLSR were larger at pH around 7 and around 9 than at pH 7.5-8. The level of ALLMR results was chosen for the proposal of the K_d values.

Table Pa-10. *The best estimate K_d (m^3/kg) values of protactinium for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite KGa-1b							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**	**1.5E+02**
10	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02	1.5E+02

Table Pa-11. *The best estimate K_d (m^3/kg) values of protactinium for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite IMt-1							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E+01**	**6.0E+01**	**6.0E+01**	**6.0E+01**	**6.0E+01**	**6.0E+01**	**6.0E+01**
10	6.0E+01	6.0E+01	6.0E+01	6.0E+01	6.0E+01	6.0E+01	6.0E+01

21.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(Pa-3)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(Pa-4)}$$

The uncertainty factors are collected in Tables Pa-12 and Pa-14. Only those factors which are greater than one are listed.

Kaolinite

UF_{tot}= 5.3. The total uncertainty factor UF_{tot} is 5.3 for all reference waters except for OLSR is 3.8.

UF_{source}= 1.9. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values. The best estimate K_d values for kaolinite were calculated from the results of OLSR. The factor 3 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1. Cation exchange capacity was not used in the calculations. The sorption capacity of the well-crystallised KGa-1b kaolinite is most probably not higher than that of the in-situ Olkiluoto kaolinite.

UF_{spec}= 1 the uncertainty of speciation for OLSR water. The K_d values were calculated from the experimental R_d values in OLSR.

UF_{spec}= 1.4 for other reference waters than OLSR.

UF_{pH}= 1. There was no effect of pH on the proposed R_d values (Figure Pa-5).
$UF_{lab/field}$= 2. The uncertainty of upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Eu for kaolinite in Olkiluoto geosphere are presented in Table Pa-13.

Illite

The total uncertainty factor UF_{tot} is 11 for all reference waters, except for ALLMR it is 7.8.

UF_{source}= 3. The uncertainty factor of source data (UF_{source}) describes the uncertainty of the experimental R_d values. The best estimate K_d values for illite were calculated from the results of ALLMR. The factor 1.9 covers the scattering of the R_d values.

UF_{model}= 1. No model was used.

UF_{CEC}= 1.3, the uncertainty factor of cation exchange capacity. The uncertainty in the source material compared with the Olkiluoto site illite is taken into account in the uncertainty factor UF_{CEC}, which was taken as 1.3, since the CEC of source data illite and Olkiluoto illite may be significantly different (Bradbury & Baeyens 2003c, Missana et al. 2008).

Table Pa-12. *The factors used for calculation of the lower limit values for kaolinite in Olkiluoto geosphere. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite				
Water	UF_{source}	UF_{spec}	$UF_{lab/field}$	UF_{tot}
OLGA	1.9	1.4	2	5.3
OLGO	1.9	1.4	2	5.3
ALLMR	1.9	1.4	2	5.3
OLBA	1.9	1.4	2	5.3
OLSR	1.9	1	2	3.8
KR4	1.9	1.4	2	5.3
KR20	1.9	1.4	2	5.3

Table Pa-13. *The lower limit K_d (m^3/kg) values of protactinium for kaolinite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.8E+01**	**2.8E+01**	**2.8E+01**	**2.8E+01**	**4.0E+01**	**2.8E+01**	**2.8E+01**
10	2.8E+01	2.8E+01	2.8E+01	2.8E+01	4.0E+01	2.8E+01	2.8E+01

UF_{spec}= 1 the uncertainty of speciation for ALLMR water. The K_d values were calculated from the experimental ALLMR results.

UF_{spec}= 1.4 for other reference waters.

UF_{pH}= 1. There was no effect of pH on the proposed R_d values (Figure Pa-6).

$UF_{lab/field}$= 2. The uncertainty of upscaling from laboratory data to whole clay matrix is covered by the factor 2.

The lower limit K_d (m^3/kg) values of Pa for illite in Olkiluoto geosphere are presented in Table Pa-17.

Table Pa-14. *The factors used for calculation of the lower limit values for illite in Olkiluoto geosphere. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite					
Water	UF_{source}	UF_{CEC}	UF_{spec}	$UF_{lab/field}$	UF_{tot}
OLGA	3	1.3	1.4	2	11
OLGO	3	1.3	1.4	2	11
ALLMR	3	1.3	1	2	7.8
OLBA	3	1.3	1.4	2	11
OLSR	3	1.3	1.4	2	11
KR4	3	1.3	1.4	2	11
KR20	3	1.3	1.4	2	11

Table Pa-15. *The lower limit K_d (m^3/kg) values of protactinium for illite at the pH of reference water (REF) and at pH 10. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite							
pH	OLGA	OLGO	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.5E+00**	**5.5E+00**	**7.7E+00**	**5.5E+00**	**5.5E+00**	**5.5E+00**	**5.5E+00**
10	5.5E+00	5.5E+00	7.7E+00	5.5E+00	5.5E+00	5.5E+00	5.5E+00

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22 NEPTUNIUM

22.1 Speciation

Neptunium (Np) has several oxidation states, of which Np(IV) and Np(V) are relevant in geosphere conditions. Speciation in the waters was calculated with the PHREEQC programme using the ANDRA Thermo_Chimie 7b TDB.

22.1.1 Saline waters

In reducing conditions in the saline KR20_465_1 water, Np(IV) hydroxo complexes $Np(OH)_3^+$ and $Np(OH)_4$ and the anionic hydroxocarbonato complex coexist. The proportion of $Np(OH)_4$ is more than 95% at the pH of the groundwater (Figure Np-1). The carbonate concentration in the OLSR water is even lower, and only hydroxo species are present (Figure Np-2). In reducing low-CO_3^- groundwaters, only $Np(IV)OH)_4$ species must be considered. The modelling suggests that the impact of carbonate and halide ions on the complexation of Np(IV) is small.

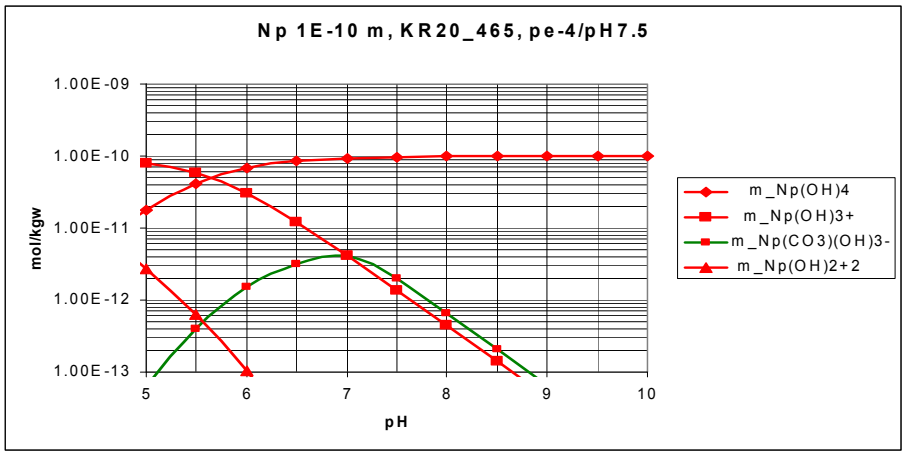

Figure Np-1. *Speciation of neptunium in saline KR20_465_1 water, pe -4.5/pH 7.5.*

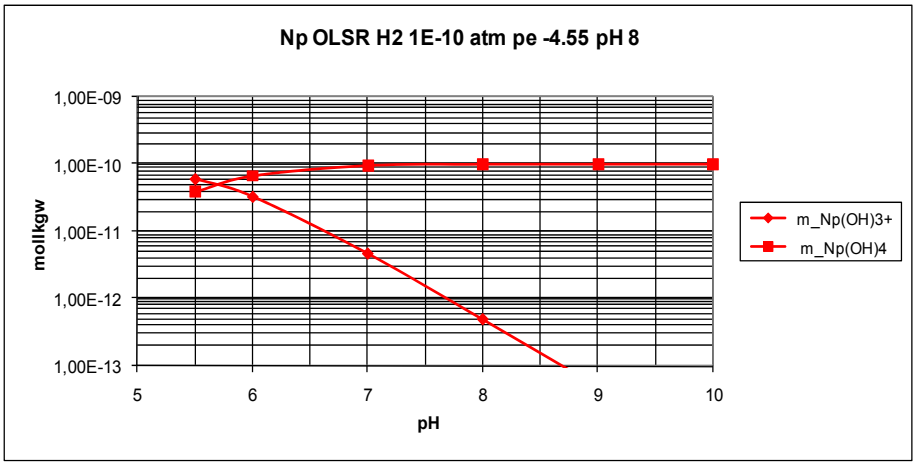

Figure Np-2*. Speciation of neptunium in saline OLSR water, pe -4.55/pH 8.0.*

22.1.2 Brackish waters

In the brackish groundwater OLBA under reducing conditions, the speciation is very much the same as in KR20_465_1 water. The anionic hydroxocarbonato complexes of Np(IV) are minor components (Figure Np-3).

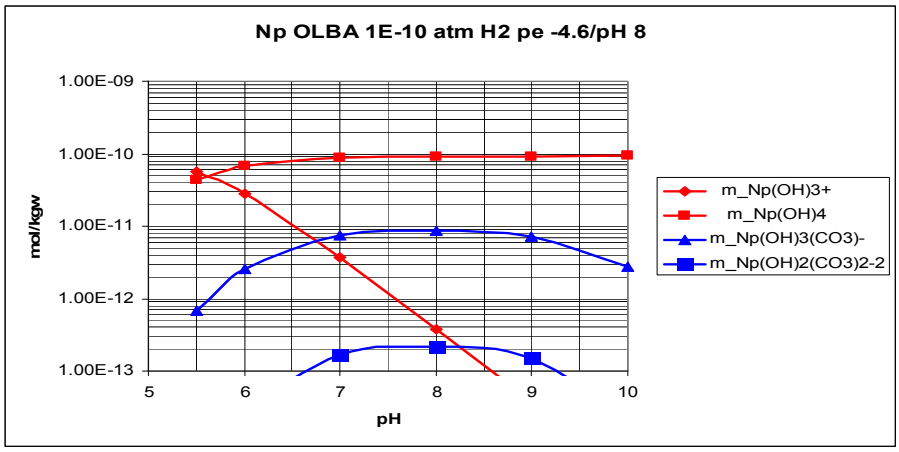

Figure Np-3. *Speciation of neptunium in brackish OLBA water, pe -4.6/pH 8.*

In the reducing brackish KR4_81_1 water, $Np(OH)_4$ is the main species with 20% contribution of the anionic hydroxocarbonato complexes between pH 7 and pH 9 (Figure Np-4).

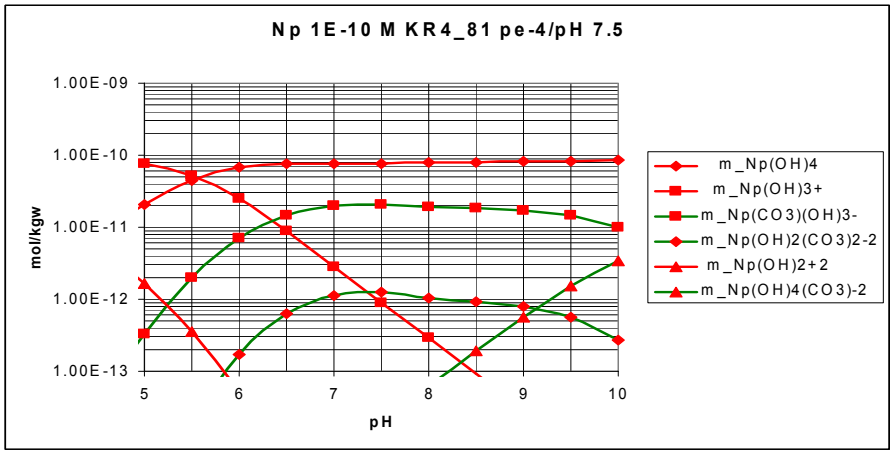

Figure Np-4. *Speciation of neptunium in brackish KR4_81_1 water, pe -4/pH 7.5.*

22.1.3 Fresh waters

In reducing fresh ALLMR water, the main species are the Np(IV) hydroxo complexes. At pH 8.8, the proportion of the $Np(OH)_4$ species is 94%, and 96% at pH 10, very much the same as in the brackish water OLBA in Figure Np-3.

22.1.4 Glacial melt water

In reducing glacial melt water OLGA, the speciation is the same as in the saline OLSR water (Figure Np-2).

In redox conditions equivalent to Grimsel water at pH 9.6, the conditions at pH 6 are mildly oxidising to Np and NpO_2^+ ion is the main species and the contribution of Np(IV) hydroxo species at pH 5.8 is about 20%. (Figure Np-5).

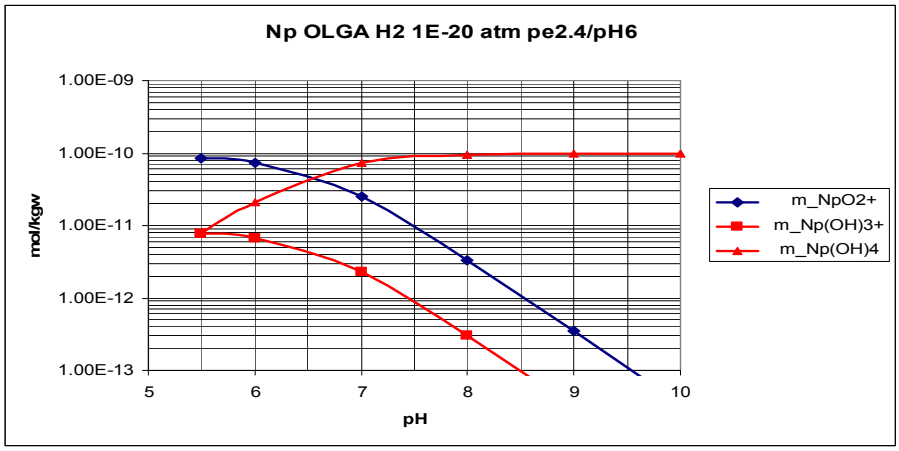

Figure Np-5. *Speciation of neptunium in glacial melt OLGA water, pe 2.4/pH 6.*

22.1.5 Aerobic waters

Np(V) is the dominating oxidation state in aerobic glacial melt water OLGO (Figure Np-6), fresh water ALLMO (Figure Np-7) and 1:10 diluted fresh aerobic groundwater simulant ALLARD used in sorption experiments (Kaukonen et al. 1997) (Figure Np-8). In the high-carbonate water KR4_81_1 (Figure Np-9), the main species would be the NpO_2^+ ion and its anionic carbonate complexes. The proportion of carbonate complexes in the waters is in direct relation to the carbonate concentration of the water.

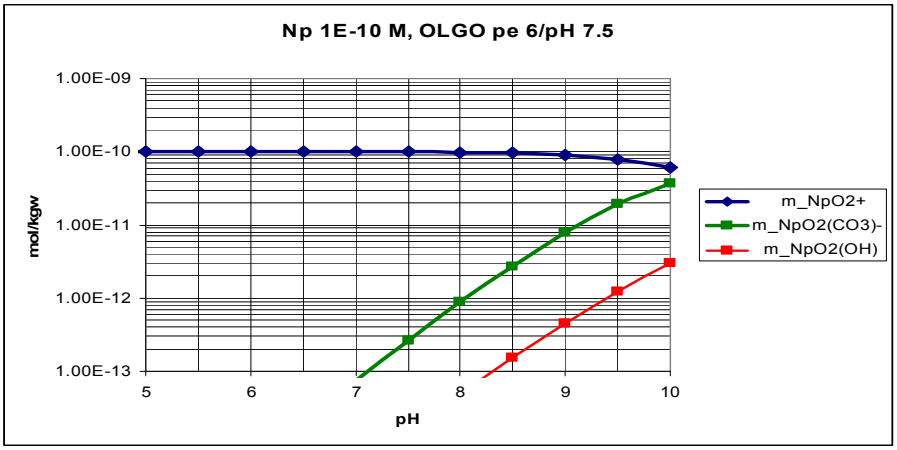

Figure Np-6. *Speciation of neptunium in the glacial melt water OLGO, pe 6/pH 7.5.*

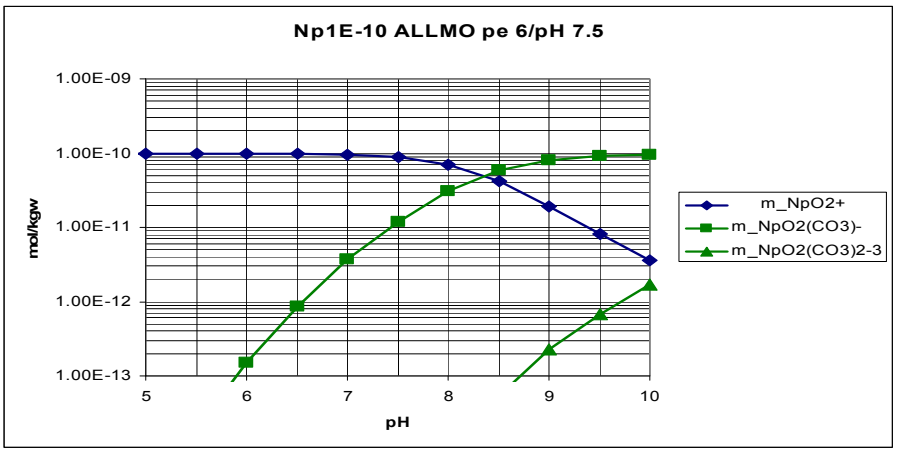

Figure Np-7. *Speciation of neptunium in the fresh ALLMO water, pe 5.5/pH 8.*

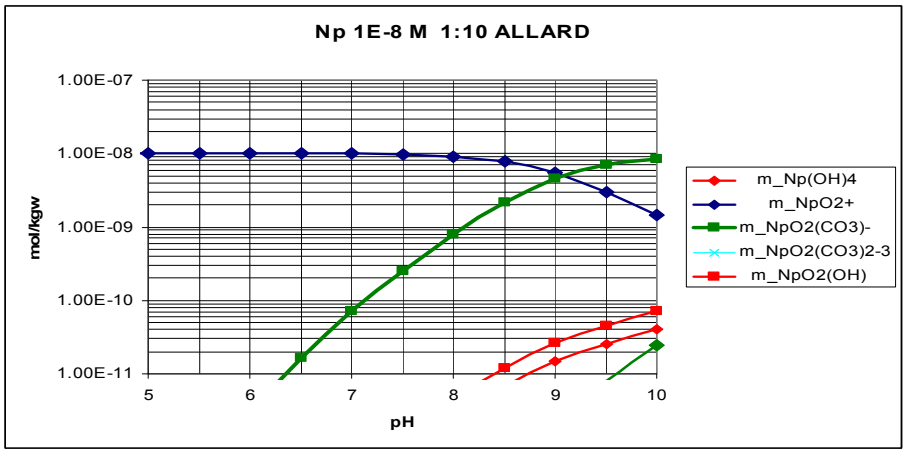

Figure Np-8. *Speciation of neptunium in 1:10 diluted ALLARD water used in sorption experiments (Kaukonen et al. 1997), pe 5.5/pH 8, 2E-4 M carbonate.*

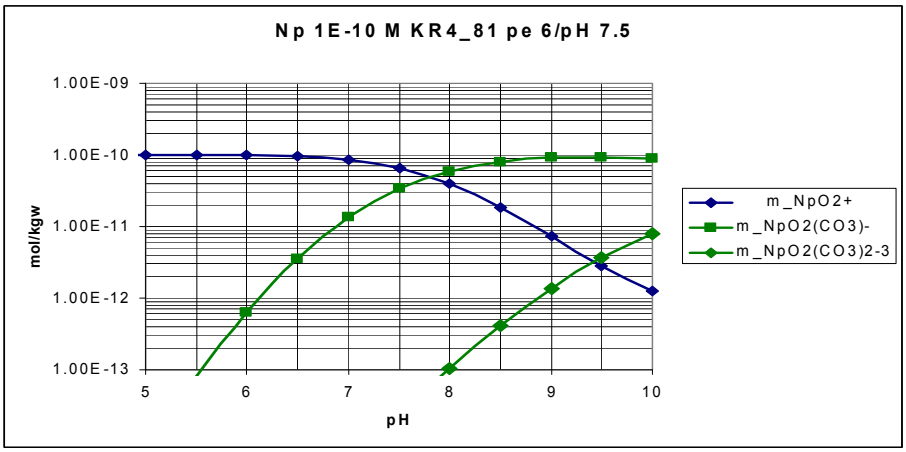

Figure Np-9. *Speciation of neptunium in aerobic KR4_81_1 type water. pe 6/pH 7.5*

22.2 Sorption on rocks

The in-house sorption experiments were all performed using carrier-free Np-235 ($t_{1/2}$=396 d) isotope as the tracer isotope, to keep the Np concentration lower than the estimated solubility of $Np(IV)(OH)_4$ also under reducing conditions. The Np-237 ($t_{1/2}$= $2.1 \cdot 10^6$ a) was used as a carrier at higher Np-concentrations in aerobic conditions.

Sorption experiments have been performed using Olkiluoto mica gneiss and pegmatite granite, Kivetty granite (Hakanen & Lindberg 1989, 1995, Kaukonen et al. 1997), Romuvaara tonalite and Kivetty granite/granodiorite (Kaukonen et al. 1993), Hästholmen rapakivigranite (Huitti et al.1996) and basic plutonic rocks (Kaukonen et al. 1993).

22.2.1 Source data in anaerobic conditions

Hakanen & Lindberg (1989) determined the sorption of Np on rock surfaces and showed that the main oxidation state under anaerobic conditions is Np(IV). The proportion of Np(IV for samples comprising of natural OLKR5 groundwater (pH 8.2, Eh -320 mV) and rock was 67 % after 40 days and 96 % after 78 days. For the Olkiluoto tonalite (36.8 % micas+amphibole), the amount of Np in water after 78 days was < 0.4 % of the total activity. Sorption higher than 99 % was found for Np that was used together with Tc as a redox indicator in samples comprising of crushed OLKR1 mica gneiss in OLKR5 brackish water (Hakanen & Lindberg 1995). The proportion of Np(IV) of total Np was higher than 96 %. These results indicate the reduction of Np(V) to Np(IV) and high sorption of Np on rocks in reducing conditions. The accuracies of determination of sorption in these experiments were not high and only a lower limit of R_d value (0.6 m^3/kg) can be derived. This value is low, compared to R_d for Th and other strongly hydrolysing tetravalent elements, and K_d values for Np(IV) must be derived from sorption of chemical analogues.

22.2.2 Source data in aerobic conditions

Kaukonen et al. (1997) determined the sorption of Np-235 under aerobic conditions on Olkiluoto crushed pegmatite granite and mica gneiss. The results for the samples that were crushed intact rock and not including surface coatings are summarised in Table Np-1.

Table Np-1. *Sorption of Np-235 under aerobic conditions on crushed Olkiluoto pegmatic granite and mica gneiss in brackish/saline aerobic OLKR5 water (Kaukonen et al. 1997).*

water	pH	Rock	biotite %	grain size mm	BET/N2 m2/g	Rd m^3/kg
OLKR5 *	8.2±0.2	peg.granite	0 - 2	< 2	0.21	$(4.4 \pm 0.3) \cdot 10^{-3}$
OLKR5 *	8.2±0.2	peg.granite	0 - 2	< 0.5	0.31	$(3.6 \pm 0.4) \cdot 10^{-3}$
OLKR5 *	8.2±0.2	mica gn.	31.8	< 2	0.44	$(2.5 \pm 0.5) \cdot 10^{-3}$
OLKR5 *	8.2±0.2	mica gn	31.8	< 0.5	0.45	$(3.6 \pm 0.4) \cdot 10^{-3}$
* aerobic carbonate-free water						

Influence of ionic strength on sorption of Np(V)

In the report by Kaukonen et al. (1997), the sorption of Np(V) on quartz, potassium feldspar, muscovite and pyrite was the same and only two times higher in on biotite pH 8.1 in the low ionic 1:10 diluted ALLARD (I.S. $3 \cdot 10^{-3}$ M) water than at around pH 8.2 in saline water (aerobic OLKR5, I.S 0.3 M). Sabodina et al. (2006) determined sorption of Np under oxidising conditions on montmorillonite in 0.01–0.1 M $NaClO_4$ solutions. There was no influence of ionic strength on the sorption at a pH higher than 7. Sorption of Np(V) on montmorillonite was inversely proportional to ionic strength at lower than pH 7, suggesting that sorption on silicate minerals at low pH conditions also takes place by cation exchange. For illite (Gorgeon 1994) sorption in 0.01 M and 0.1 M, ionic strength was assumed to have no influence on the K_d values of Np(V) on the rocks in the groundwaters. These results support the estimation that sorption of Np(V) at pH 8 takes place mainly by surface complexation.

Sorption of Np(V) in waters containing carbonate (CO_3^-)

The glacial melt water OLGO and fresh water ALLMO contain carbonates. The speciation in closed aerobic conditions for OLGO, and ALLMO waters indicate that the NpO_2^+ ion is the main species for the whole pH range for the glacial melt water. The proportion of the NpO_2^+ ion is 100 % in OLGO, 85 % in ALLMO and 50 % in KR4_81_1.

The effect of carbonate concentration on sorption of Np on basic crystalline rocks was measured in Kaukonen et al. (1993). The R_d values for crushed (BET/N_2 0.4 m^2/g) Syyry plutonic rock in low ionic strength solution with different total carbonate concentration at pH 8 had ranges $5.4 \cdot 10^{-2}$ -$1.34 \cdot 10^{-1}$ m^3/kg in < 2 mg/L carbonates, $2.0 \cdot 10^{-2}$-$6.0 \cdot 10^{-2}$ m^3/kg in 12.3 mg/L carbonates and $1.4 \cdot 10^{-2}$ –$2.1 \cdot 10^{-2}$ m^3/kg in 123 mg/L carbonates (equilibrium with ambient atmosphere) The R_d values indicate that sorption in waters of low carbonate concentration was higher than under ambient atmospheric concentrations, but the difference at pH 7–8 was not large. Sorption of Np(V) on kaolinite in CO_2-free and under ambient atmospheric conditions was the same up to pH 8.5 in Amayri et al. (2004) and Jermolajev et al. (2005), but decreased at higher pH (see Np(V) sorption on kaolinite). Under CO_2 partial pressure of $10^{-3.5}$ atm (ambient atmosphere) for montmorillonite, the R_d value was $8 \cdot 10^{-2}$ m^3/kg at pH 8 and $5 \cdot 10^{-2}$ m^3/kg at pH 9.5 and $2 \cdot 10^{-2}$ m^3/kg at pH 10, as extrapolated from the Figures in Turner et al. (1998). These results above suggest that sorption on rocks in groundwater is decreased by carbonate complexation of Np(V) only in the waters at pH 10 in this report. The values for kaolinite (Amayri et al. 2004) at pH 9 are about 4.5 times higher than at pH 8 and under aerobic CO_2 pressure about the same at pH 8 and at pH 10. The increase of sorption of NpO_2^+ with pH in CO_2-free conditions and decrease of free NpO_2^+ concentration results in the fact that in aerobic conditions the best estimate K_d value at pH 10 is the same as at pH 8.

Influence of pH on sorption of Np(V)

The R_d value for sorption on kaolinite at pH 6 was 1/40 times that at pH 8, under both CO_2^-free and atmospheric conditions (Amayri et al. 2004). For montmorillonite, the

ratio in CO_2^- free conditions was about 1/10 (Bradbury and Baeyens 2005) and about 1/4 for illite (Gorgeon 1994). In CO_2^- free conditions, the R_d value for montmorillonite at pH 10 was about 4 times and for illite 10 times higher than at pH 8.

As the conservative approach the authors selected to use the ratio 1/40 determined for kaolinite to reduce the values for the glacial melt water OLGO at pH 5.8, due to the low CEC of the rocks. So as not to overestimate sorption, the K_d values in OLGO at pH 10 are estimated to be 4 times those at pH 8. In the carbonate-containing water ALLMO, the K_d values at pH 10 are proposed to be the same as at pH 8.

22.2.3 Best estimate K_d values

Best estimate K_d values in anaerobic/reducing conditions

The in-house sorption results of Np indicate a reduction of Np(V) to Np(IV) in anaerobic groundwater conditions at Olkiluoto, and high sorption of Np(IV). The accuracy of measured sorption did not allow the estimation of relevant K_d values for Np(IV). Hence, the K_d values of Np(IV) for the rocks were derived from the sorption of Th(IV) as an analogue to Np(IV).

According to the LFER theory shown for sorption on montmorillonite and on illite (Bradbury & Baeyens 2005, 2009), the sorption of the hydroxo complexed tri-valent and tetra-valent metal ions is higher the larger the hydrolysis constants for the species. This suggests that sorption of Np(IV) in the reference waters on aluminosilicate minerals is higher than that of Th(IV) but lower than that of Sn(IV).

The pH dependence of R_d values of Np in anaerobic conditions indicate that there is no sharp pH edge in the sorption of Np(IV) (Nagasaki et al. 1999). Similarities in the complexation of Np(IV) and Th and the LFER relationship indicate that the use of K_d values of Th to Np(IV) does not overestimate the sorption of Np in anaerobic conditions. It follows that the same K_d values as for Th(IV) are suggested for Np(IV) (Table Np-2 – Np-5)

Table Np-2. *Best estimate K_d values (m^3/kg) of neptunium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**	**8.0E+00**
10	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00	8.0E+00

Table Np-3. *Best estimate K_d values (m^3/kg) of neptunium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Np-4. *Best estimate K_d values (m^3/kg) of neptunium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**	**4.0E+00**
10	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00	4.0E+00

Table Np-5. *Best estimate K_d values (m^3/kg) of neptunium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-01**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**	**1.0E+00**
10	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00	1.0E+00

Best estimate K_d values in aerobic conditions

The K_d value $6 \cdot 10^{-4}$ m^3/kg ($3.0 \cdot 10^{-3}$ m^3/kg*0.26/.33*0.23= $6.0\ 10^{-4}$ m^3/kg) for T-MGN in aerobic conditions at pH 8 was calculated for T-MGN rock from the mean of R_d value to mica gneiss in aerobic OLKR5 water in Table Np-1. The conversion factors were the mica contents of the rocks and the crushed rock to intact rock conversion factor. The K_d values for other rocks are related to the K_d value of T-MGN by the proportions of the R_d to K_d conversion factors for the rocks. K_d in OLGO is calculated to 1/40 times the Kd at pH 8 and at pH 10 4 times the K_d value at pH 8. The K_d at pH 7.2 in OLSO is estimated to 1/10 times the K_d in ALLMR (pH 8.4) as proposed by the pH dependency in sorption to kaolinite. At pH 10, the sorption in OLSO is the same as in OLGO at pH 10. In carbonate-containing ALLMO, sorption at pH 10 is estimated to be the same as at pH 8.The best estimate values are given in Tables Np-6 – Np-9.

Table Np-6. *Best estimate K_d values(m^3/kg) of Np(V) for T-MGN in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

T-MGN			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-05**	**6.0E-04**	**6.0E-05**
10	2.0E-03	6.0E-04	2.0E-03

Table Np-7. *Best estimate K_d values(m^3/kg) of Np(V) for P-TGG in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

P-TGG			
pH	OLGO	ALLMO	OLSO
REF	**1.0E-05**	**3.0E-04**	**3.0E-05**
10	1.0E-03	3.0E-04	1.0E-03

Table Np-8. *Best estimate K_d values(m^3/kg) of Np(V) for T-TGG in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

T-TGG			
pH	OLGO	ALLMO	OLSO
REF	**8.0E-06**	**3.0E-04**	**3.0E-05**
10	1.0E-03	3.0E-04	1.0E-03

Table Np-9. *Best estimate K_d values(m^3/kg) of Np(V) for PGR in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

PGR			
pH	OLGO	ALLMO	OLSO
REF	**4.0E-06**	**1.0E-04**	**1.0E-05**
10	4.0E-04	1.0E-04	4.0E-04

22.2.4 Lower limit K_d values

Lower limit K_d values in anaerobic/reducing conditions

For the same reason as for the proposal of best estimate values, the same lower limit K_d values as for Th are proposed (Table Np-10 – Np-13).

Table Np-10. *Lower limit K_d values (m^3/kg) of neptunium for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**	**4.0E-01**
10	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01	4.0E-01

Table Np-11. *Lower limit K_d values (m^3/kg) of neptunium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-02**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Np-12. *Lower limit K_d values (m^3/kg) of neptunium for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E-02**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**	**2.0E-01**
10	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01	2.0E-01

Table Np-13. *Lower limit K_d values (m^3/kg) of neptunium for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**	**2.0E-02**
10	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02	2.0E-02

Lower limit K_d values in aerobic conditions

The factor due to mineralogical uncertainties is 18. The uncertainty in the estimation of species is less than the mineralogical uncertainty. For K_d values at pH 10, the uncertainties additionally include the effects of carbonates on sorption. It is regarded as reasonable to use an uncertainty factor of 20 for T-MGN, P-TGG and T-TGG and a factor of 50 for PGR (Table Np-14. The lower limit values are given in Tables Np-15 – Np-18.

Table Np-14. *Uncertainty factors for the lower limit K_d values of Np(V) for the Olkiluoto rocks.*

Rock	UF
T-MGN	20
P-TGG	20
T-TGG	20
PGR	50

Table Np-15. *Lower limit K_d values (m^3/kg) of Np(V) for T-MGN in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

T-MGN			
pH	OLGO	ALLMO	OLSO
REF	**1.0E-06**	**3.0E-05**	**3.0E-06**
10	1.0E-04	3.0E-05	1.0E-04

Table Np-16. *Lower limit K_d values (m^3/kg) of Np(V) for P-TGG in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

P-TGG			
pH	OLGO	ALLMO	OLSO
REF	**5.0E-07**	**2.0E-05**	**2.0E-06**
10	5.0E-05	2.0E-05	5.0E-05

Table Np-17. *Lower limit K_d values(m^3/kg) of Np(V) for T-TGG in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

T-TGG			
pH	OLGO	ALLMO	OLSO
REF	**4.0E-07**	**2.0E-05**	**4.0E-05**
10	4.0E-05	2.0E-05	2.0E-06

Table Np-18. *Lower limit K_d values(m^3/kg) of Np(V) for PGR in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

PGR			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-08**	**2.0E-06**	**2.0E-07**
10	2.0E-06	2.0E-06	2.0E-06

22.3 Sorption on clays

22.3.1 Sorption of Np(IV) on clays

No data for sorption of Np(IV) on clays in reducing conditions was found. In accordance with sorption on rocks, the same best estimate(Table Np-19 – Np-21) and lower limit K_d values (Table Np-22 – Np-24as for Th on clays are proposed.

Table Np-19. *Best estimate K_d values (m^3/kg) of neptunium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E+01**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**
10	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02	2.0E+02

Table Np-20. *Best estimate K_d values (m^3/kg) of neptunium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**
10	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01	2.0E+01

Table Np-21. *Best estimate K_d values (m^3/kg) of neptunium for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

	Chlorite					
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+02**	**3.0E+02**	**3.0E+02**	**3.0E+02**	**3.0E+02**	**3.0E+02**
10	3.0E+02	3.0E+02	3.0E+02	3.0E+02	3.0E+02	3.0E+02

Table Np-22. *Lower limit K_d (m^3/kg) values of neptunium for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E+01**	**8.4E+01**	**8.3E+01**	**8.4E+01**	**6.0E+01**	**6.0E+01**
10	8.4E+01	8.4E+01	8.4E+01	8.4E+01	6.0E+01	6.0E+01

Table Np-23. *Lower limit K_d (m^3/kg) values of neptunium for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E+00**	**7.5E+00**	**7.5E+00**	**7.5E+00**	**5.3E+00**	**5.3E+00**
10	7.5E+00	7.5E+00	7.5E+00	7.5E+00	5.3E+00	5.3E+00

Table Np-24. *Lower limit K_d (m^3/kg) values of neptunium for chlorite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Chlorite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.5E+01**	**9.9E+01**	**9.9E+01**	**9.9E+01**	**7.0E+01**	**7.0E+01**
10	9.9E+01	9.9E+01	9.9E+01	9.9E+01	7.0E+01	7.0E+01

22.3.2 Source data to sorption in aerobic conditions

Kaolinite

The sorption of Np(V) on KGa-1b kaolinite was determined by Amayri et al. (2004a, 2005) and Jermolajev et al. (2005) in $NaClO_4$ solutions in CO_2-free and ambient atmospheric conditions. Niitsu et al. (1997) determined sorption on a Japanese kaolinite (Iwamoto mineral Co) under an N_2 atmosphere. The R_d values of Np(V) were converted from the percentage sorption data graphs for the KGa-1b kaolinite and from the data of Niitsu et al. (1997). The R_d values in Niitsu et al. (1997) were divided by two due to the fact that the BET/N_2 surface area of the Japanese kaolinite was 24.5 m^2/g, about two times that of KGa-1b. The R_d values in CO_2-free conditions are presented in Figure Np-10, and in Figure Np-11 for ambient atmosphere conditions.

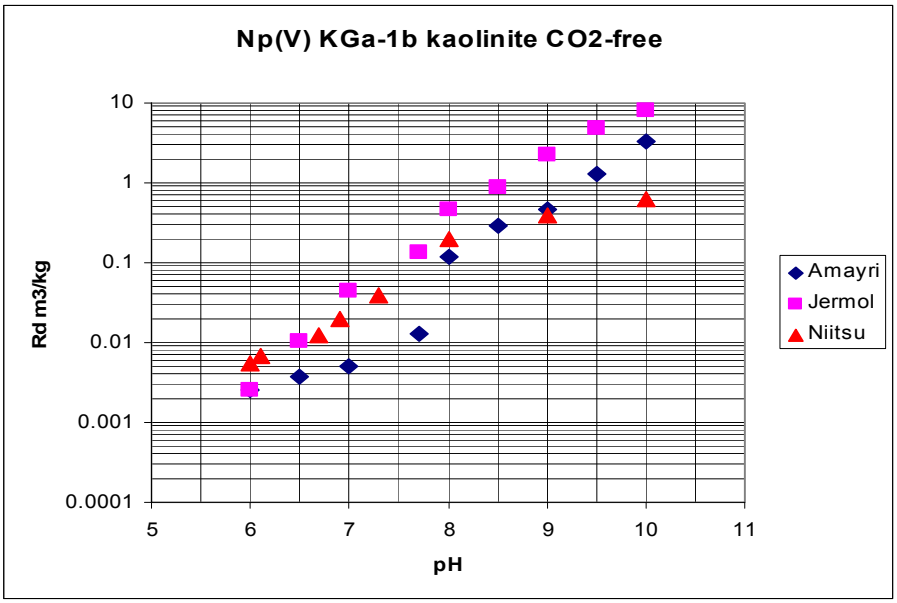

Figure Np-10. *R_d values of Np(V) for kaolinite in 0.1 M $NaClO_4$ CO_2-free solution. The data labels indicate the source data of reference (Amayri et al. 2004, Jermolajev et al. 2005, Niitsu et al. 1997).*

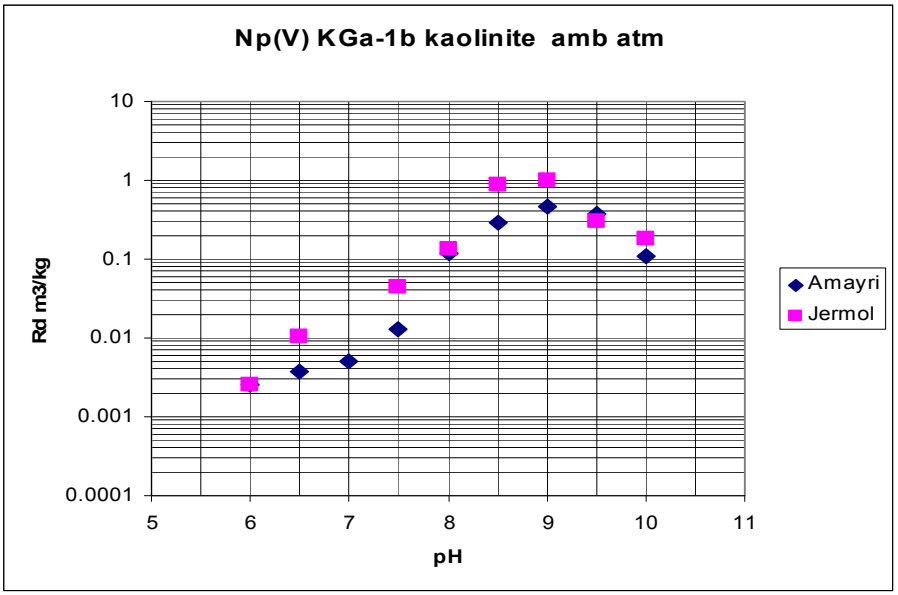

Figure Np-11. *R_d values of Np(V) for kaolinite in 0.1 M $NaClO_4$ solution under ambient atmosphere. The data labels indicate the references of the data. (Jermolajev et al.2005, Amayri et al. 2004).*

Under ambient atmospheric conditions, the K_d values are reduced due to carbonate complexation of Np(V) only at pH 8.5 and higher. Speciation of Np(V) in fresh ALLMO water gives the result that at pH 8.4 about 50 % of neptunium is as NpO_2^+ and 50% as anionic carbonato complexes. For the best estimate, the authors rely more on the experimental values that indicate that sorption under ambient atmospheric conditions at pH 8.4 is the same or higher than that under CO_2-free conditions. Sorption on kaolinite is not sensitive to Na concentration of the solution, as indicated by the same sorption in 0.01 M and 0.1 M $NaClO_4$ in Amayri et al. (2005), on biotite in the saline water OLKR5 (pH 8.2) and in 1:10 diluted fresh ALLMO water (pH 8.1) (Kaukonen et al. 1997).

pH 10

At pH 10 in ALLMO water the calculated proportion of NpO_2^+ ion is 3.6 %. The R_d values of 3.3 m^3/kg and 8–9 m^3/kg could be suggested from graphs in Amayri et al. (2004) and Jermolajev (2005). In ALLMO at pH 10, the R_d values of $1.1 \cdot 10^{-1}$ m^3/kg and $2.9 \cdot 10^{-1}$ m^3/kg can be suggested from the R_d values of 3 m^3/kg and 8 m^3/kg at pH 10 in CO_2-free conditions (Figure Np-10), assuming that 3.6 % of the Np species are sorbing.

Illite

Sorption of Np(V) on illite in CO_2-free 0.025 M and 0.1 M $NaClO_4$ was measured by Gorgeon (1994) and is presented as a graph in Bradbury & Baeyens (2009b). R_d values in CO_2-free conditions were adopted from the graph in Bradbury and Baeyens (2009b).

In aerobic OLGO water the dominating (>98 %) solution species is the NpO_2^+ ion at pH 5.8 and at pH 10. In ALLMO water 50 % of Np is as NpO_2^+ ion. As suggested by sorption on kaolinite, no reduction in R_d values due to carbonate was made at nominal pH of the waters. At pH 10 in ALLMO the anionic carbonate complexes are the main species and the proportion of NpO_2^+ is 3.6 %. Only the NpO_2^+ ion is assumed to be sorbing. The R_d values at pH 10 in aerobic waters were derived by multiplying the R_d value of Np(V) in CO_2-free conditions at pH 10 by the proportion of NpO_2^+ ion in the waters e.g. in ALLMR R_d (1.0 m^3/kg) to ALLMO at pH 10 is 0.036 * 1 m^3/kg = 3.6 $10^{-2}m^3$/kg

22.3.3 Best estimate K_d values of Np(V) for clays

The best estimate K_d values of Np(V) for kaolinite are presented in Table Np-25.

Kaolinite

Table Np-25. *Best estimate K_d values(m^3/kg) of Np(V) for kaolinite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

Kaolinite			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-03**	**2.0E-01**	**2.0E-02**
10	3.0E+00	1.0E-01	3.0E+00

Illite

The best estimate K_d values of Np(V) for illite are presented in Table Np-26.

Table Np-26. *Best estimate K_d values(m^3/kg) of Np(V) for illite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

Illite			
pH	OLGO	ALLMO	OLSO
REF	**1.4E-02**	**5.0E-02**	**1.6E-02**
10	1.0E+00	4.0E-02	1.0E+00

22.3.4 Lower limit K_d values of Np(V) for clays

The overall uncertainty factor (UF_{tot}) for intact fracture clays is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

$$UF_{tot} = UF_{source} * UF_{ionic} * UF_{spec} * UF_{pH} * UF_{lab/field} \quad \text{(Np-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing the best estimate K_d(BE) by its overall uncertainty factor UF_{tot}:

K_d (LL) = K_d(BE)/UF_{tot} (Np-2)

Only those factors which are greater than one are listed.

Kaolinite

The total uncertainty factors UF_{tot} of neptunium Np(V) for kaolinite in Olkiluoto are 9 for OLGA, 13 for ALLMO pH 8.4, 9 for ALLMO pH 10 and 9 for OLSO reference waters (Table Np-27). The lower limit values are given in table Np-28.

$UF_{source\ data}$ = 2. Sorption data to KGa-1b measured in Mainz University was used. The K_d values suggested from the graphs in the papers differ. A UF factor of around two is needed to cover the results.

UF_{spec} =1.4 for OLGA and OLSO as the only solution species is the NpO_2^+ ion.

UF_{spec} =2 for ALLMO at pH 8.4. Uncertainties in calculated speciations between the $NaClO_4$ solutions and the groundwaters is a potential source of error at pH 7 and higher. In speciation results for ALLMO, 50% of Np(V) is as NpO_2^+ and 50% as carbonate complexes. For the best estimate values, the experimental sorption values were used and no reduction due to anionic complexation was made.

UF_{spec} (pH 10) = 1.4 The experimental values at pH 10 in ambient atmospheric conditions are about the same as the values for ALLMO, despite the fact that the carbonate concentration is higher in the inert electrolyte solution. No larger uncertainty factor is needed.

UF_{pH} = 1.6 This value was adopted for the sorption at pH of sorption edge

UF_{ionic} (ionic strength) = 1. The fact that the same sorption in 1:10 diluted ALLMO and OLSO on biotite at around pH 7.5–8 and in 0.01 M and 0.1M $NaClO_4$ at pH 5–10 on kaolinite have been measured indicates that there is no effect of ionic strength on the sorption on kaolinite.

$UF_{lab/field}$ =2. For the K_d values measured to KGa-1b kaolinite, it is assumed that the Olkiluoto kaolinite may have only half of the sorption capacity of dispersed KGa-1b.

Illite

The total uncertainty factor UF_{tot} of neptunium Np(V) for illite in Olkiluoto is 2*2.26*1.4*2= 13. The lower limit K_d values of Np(V) for illite are shown in Table Np-29.

The uncertainty factor of the source data UF_{sd} is 2. The ratio between the mean and lower limit is about 2 in 0.025 M $NaClO_4$ used for OLGA and ALLMO and 2 in 0.1 M $NaClO_4$ used for OLSO.

Table Np-27. *The factors used for calculation of the lower limit K_d values of Np(V) for kaolinite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters. To OLGO and OLSO at pH 10 the same UF values are used as at reference pH.*

Water	UF_{source}	UF_{spec}	UF_{pH}	$UF_{lab/field}$	UF_{tot}
OLGO	2	1.4	1.6	2	9
ALLMO	2	2	1.6	2	13
ALLMO pH 10	2	2	1.6	2	13
OLSO	2	1.4	1.6	2	9

Table Np-28. *Lower limit K_d values of Np(V) for kaolinite in Olkiluoto geosphere in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

Kaolinite			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-04**	**2.0E-02**	**2.0E-03**
10	3.0E-01	1.0E-02	3.0E-01

UF_{pH} = 2.26, pH of waters coincides with the sorption edge.

UF_{spec} = 1.4. No experimental sorption values were found for Np(V) on illite in carbonate-containing waters. Sorption on kaolinite was in fair agreement with the estimated speciation of Np. No larger UF_{spec} coefficient is assumed necessary.

$UF_{lab/field}$ = 2 to cover the uncertainty between KGa-1b and Olkiluoto kaolinite.

Table Np-29. *Lower limit K_d values of Np(V) for illite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO and at pH of 10 in the waters.*

Illite			
pH	OLGO	ALLMO	OLSO
REF	**1.0E-03**	**4.0E-03**	**1.0E-03**
10	1.0E-01	3.0E-03	1.0E-01

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23 URANIUM

Uranium is redox sensitive and exists as U(IV) and U(VI) in the geosphere. In the Olkiluoto groundwaters, the maximum uranium concentration was $2.3 \cdot 10^{-8}$ M, while the median was $5.5 \cdot 10^{-9}$ M (Hellä et al. 2014).

23.1 Speciation

Speciation calculations were made using the ANDRA Thermo_Chimie Version 7b database (ANDRA 2009). Thermo_Chimie Version 7b TDB was complemented by the addition of formation constants of U(VI) alkaline-earth-carbonato complexes. The updated NEA (Nuclear Energy Agency) TDB of uranium (Guillamont et al. 2003) acknowledged these complexes but did not accept these complexes to the NEA TDB. Recently, however, Dong & Brooks (2006, 2008) published values for the formation constants for these complexes that are in agreement with the earlier values (Bernhard et al. 1996, 2001), and Prat et al. (2009) identified these complexes in waters from Finnish drill wells using fluorescence spectroscopy. In carbonate-containing oxidising to mildly reducing groundwaters, these ternary complexes are most probably the main U(VI) species (Wan et al. 2005, Stewart et al. 2010). Only in low-pH waters and highly reducing low-carbonate waters are these complexes minor.

Recently, Nair & Broder (2011) reported a clear impact of alkaline earth metals on the aqueous speciation of U(VI) and sorption on quartz. In addition, Schmeide et al. (2011) concluded that Ca-uranyl complex can contribute an enhanced mobility of U(VI) in Opalinus clay rock. These findings support the use of stability constants for ternary earth alkaline uranyl carbonate complexes in this far-field evaluation. The solubility of uranium in carbonate rich waters can be high. In Finland, there are several wells containing a high concentration of uranium, the highest being $8 \cdot 10^{-6}$M.

Leavitt et al. (2011) have recently reported their uncertainty propagation of the speciation of uranium in high carbonate groundwaters. They calculated high dissolved U concentration with decreasing U concentration, edge value $3 \cdot 10^{-6}$M of U(VI). The dissolved U(VI) concentration decreases from $5 \cdot 10^{-6}$M to $5 \cdot 10^{-8}$M when U(VI) concentration moves from $4 \cdot 10^{-6}$M to $3 \cdot 10^{-6}$M. The uncertainty in uranium speciation in high carbonate waters was confirmed. The authors find that it would be better to use more conservative values, e.g. higher solubility values, for uranium in Ca-carbonate rich waters.

Thermo_Chimie Version 7b TDB includes the $U(V)O_2^+$ ion and its carbonato complexes but no other complexation. U(V) is most probably unstable in groundwaters.

Uranium in glacial meltwater

Speciation was calculated in low-carbonate glacial meltwater in reducing OLGA (Figure U-1), mildly reducing OLGA (Figure U-2) and in oxidising meltwater OLGO (Figure U-3). Only in very reducing conditions is U(IV) the main oxidation state at pH 5.8. In low carbonate water, the hydroxo complexes of U(IV) and U(VI) are important. The speciation is highly affected by carbonate concentration. In Figure U-3, speciation is

calculated assuming carbonate alkalinity of 0.0027 meq at pH 6. In this water, the main species at pH 6 is the $UO_2(CO_3)$-complex, and at higher pH the U(VI)-alkaline-earth-carbonato complexes.

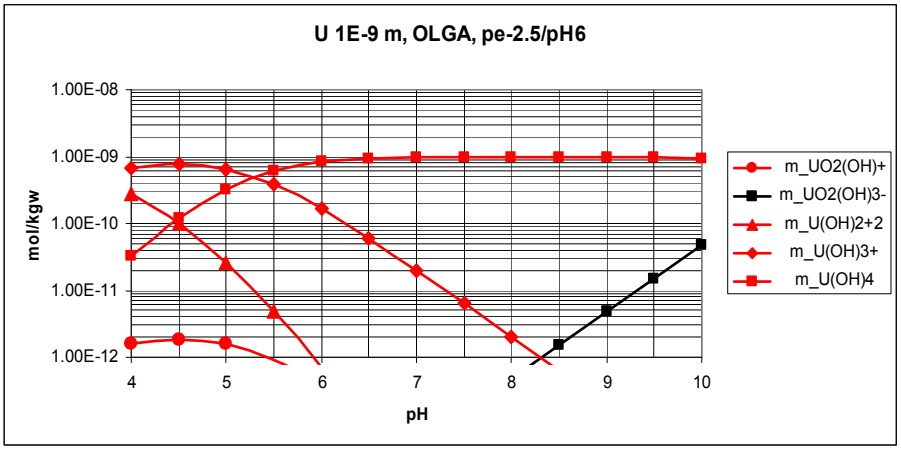

Figure U-1. *Speciation of U in low carbonate (total inorganic C 0.0027 mM) glacial meltwater OLGA in reducing conditions.*

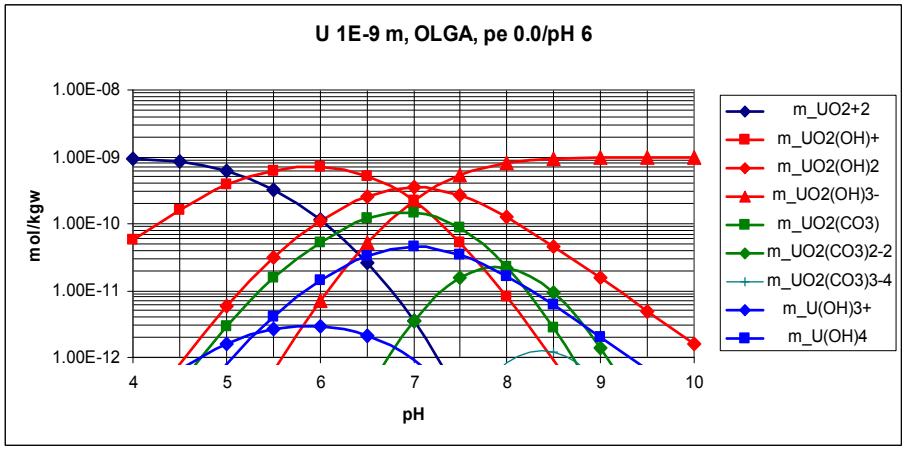

Figure U-2. *Speciation of U in low carbonate (total inorganic C 0.0027 mM) glacial meltwater OLGA in mildly reducing conditions.*

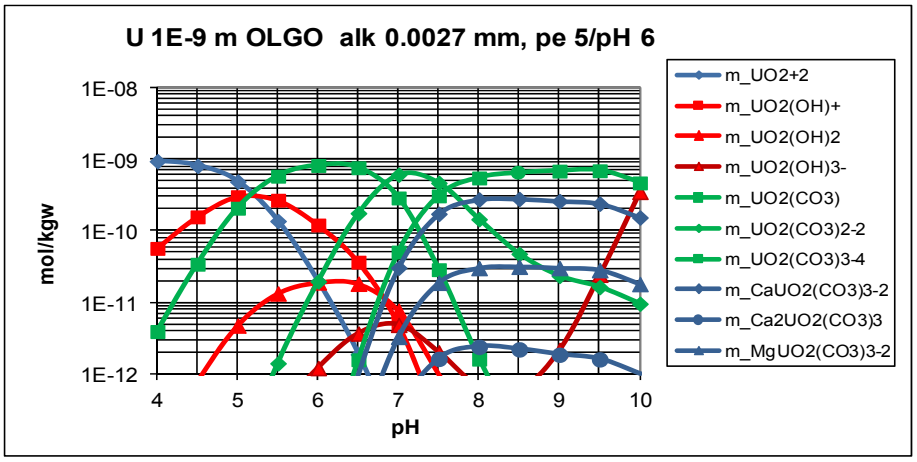

Figure U-3. *Speciation of U in glacial meltwater OLGO in oxidising conditions at carbonate alkalinity 0.0027 meq at pH 6.*

Uranium in fresh water

Speciation was calculated for mildly reducing ALLMR (Figure U-4), reducing ALLMR and oxidising ALLMO reference waters (Figure U-5). In oxidising conditions the total carbonate concentration was also varied. At higher pH, the carbonate concentration in the calculation was limited by allowing the precipitation of calcite. The carbonate and Ca concentrations in the fresh waters mean that the Ca-uranyl-carbonato complexes move the reduction of U(VI) to U(IV) at low pe values. For clearly negative E_h values and higher at pH 7.5, the main oxidation state is U(VI), and alkaline-earth-uranylcarbonato complexes are the main species, and U(IV) is present only at trace proportions. The situation at pH 8-9 is almost identical in anoxic ALLMR (Figure U-4) and in oxic (Figure U-5) conditions. Only in strongly reducing ALLMR reference water is uranium mostly at the oxidation state U(IV). The U(IV)/U(VI) ratio at around pH 8 decreases with the increase of carbonate concentration.

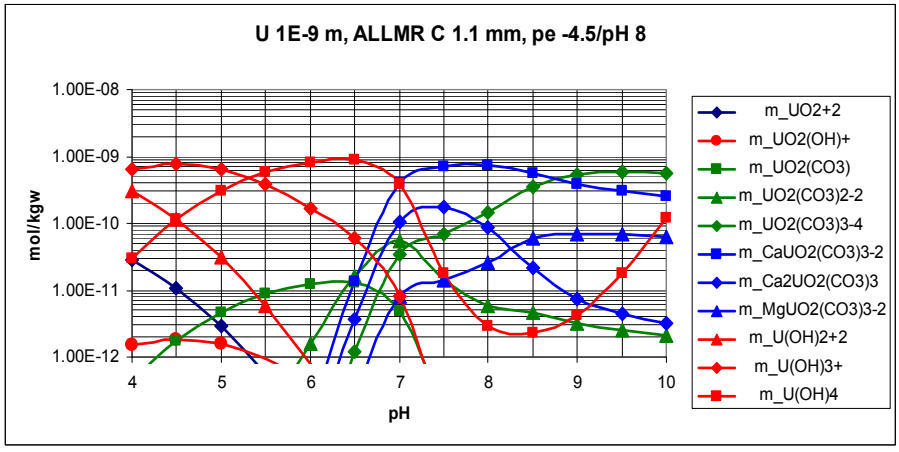

Figure U-4. *Speciation of U in fresh ALLMR reference water at pe -4.5/pH 8 with 1.1 mM total carbonate.*

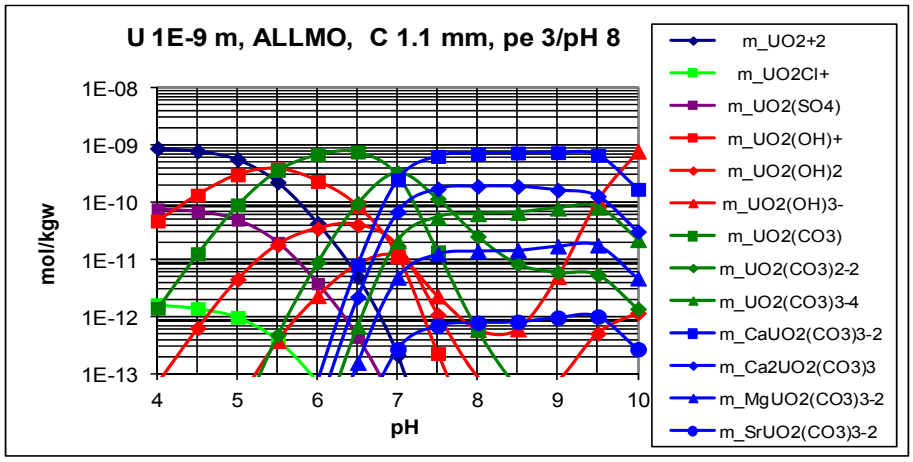

Figure U-5. *Speciation of U in fresh ALLMO reference water at pe 3/pH 7.5 with 1.1 mM total carbonate.*

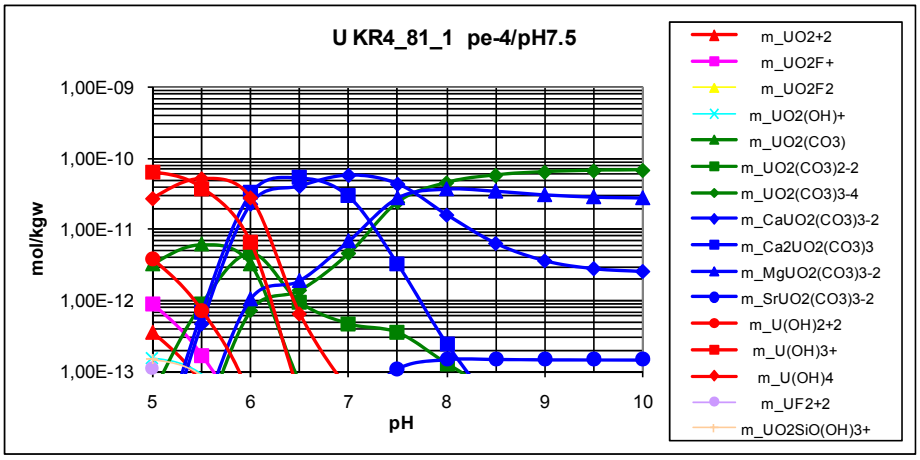

Figure U-6. *Speciation of U in brackish groundwater KR4_81_1.*

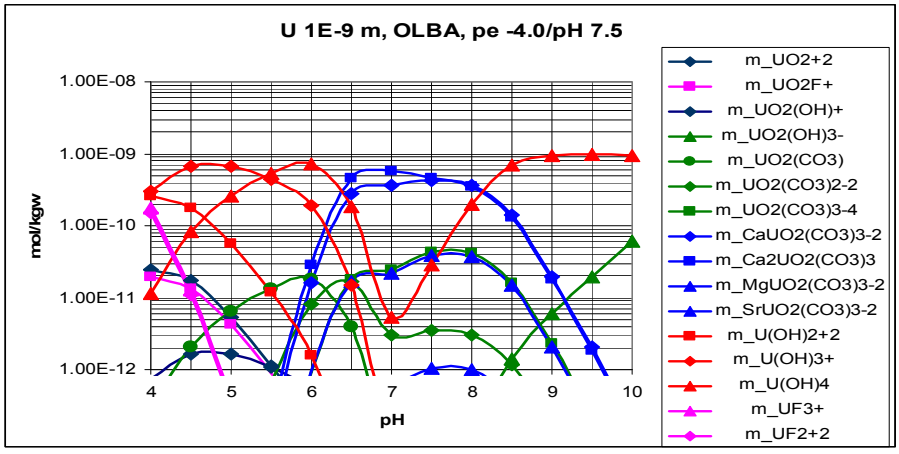

Figure U-7. *Speciation of U in brackish OLBA reference water at pe -4.0/pH 7.5.*

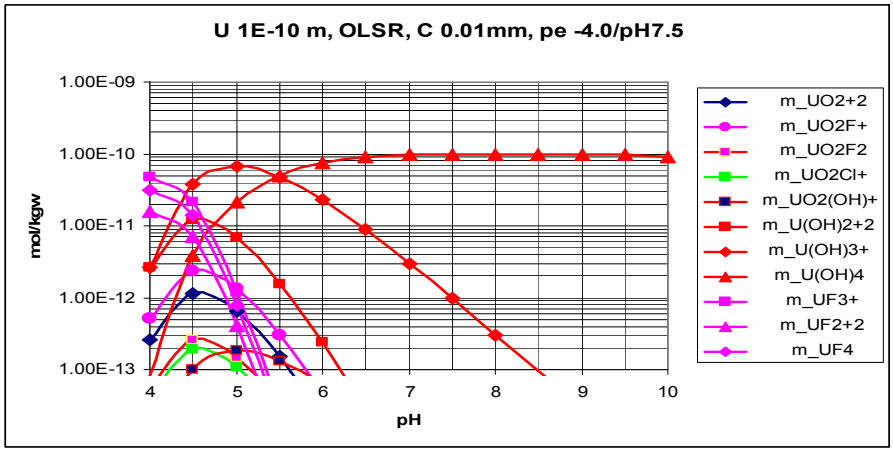

Figure U-8. *Speciation of U in nearly carbonate-free saline OLSR reference water.*

Uranium in brackish water

The speciation of uranium in brackish groundwater KR4_81_1 is shown in Figure U-6. The anionic calcium-uranyl-carbonato and uranyl-carbonato complexes dominate at pH 7 and higher.

Speciation in brackish OLBA (KR6_135_8 groundwater) reference water was calculated in reducing and mildly reducing conditions (Figure U-7). The carbonate concentration in the calculations was limited by allowing the precipitation of alkaline-earth carbonates. The high carbonate and calcium concentrations were followed by the result that in the neutral pH, the Ca-uranyl-carbonato complexes are the main species. The results suggest that U(IV) is the main oxidation state at pH 7.5 only when the pe is -5 or lower. As in the fresh ALLMR reference water at pe -1.5 and higher and at pH 7.5, the U(VI) complexes are dominating.

Uranium in saline water

Speciation in low-carbonate saline OLSR reference water was calculated for reducing (Figure U-8) to mildly reducing conditions (Figure U-9). For the reducing waters, the speciation was calculated for the total carbonate concentration of 0.01 mM, and for the mildly reducing waters also using 0.1 mM total inorganic carbon. The pe was varied from -5 to -1.5 at pH 7.5. At high pH, the carbonate concentration was allowed to be limited by the precipitation of calcite and magnesite. The high alkaline-earth ion concentration of the saline OLSR reference water is followed by the result that the Ca-uranyl-carbonato complexes become important in neutral pH values. At pe -2.8 at pH 7.5, the concentrations of $U(OH)_4$ and U(VI) complexes are about equal. In less reducing conditions, the alkaline-earth uranyl complexes become more abundant. When the carbonate concentration is suppressed to very low values, the U(VI) hydroxo complexes are the main species.

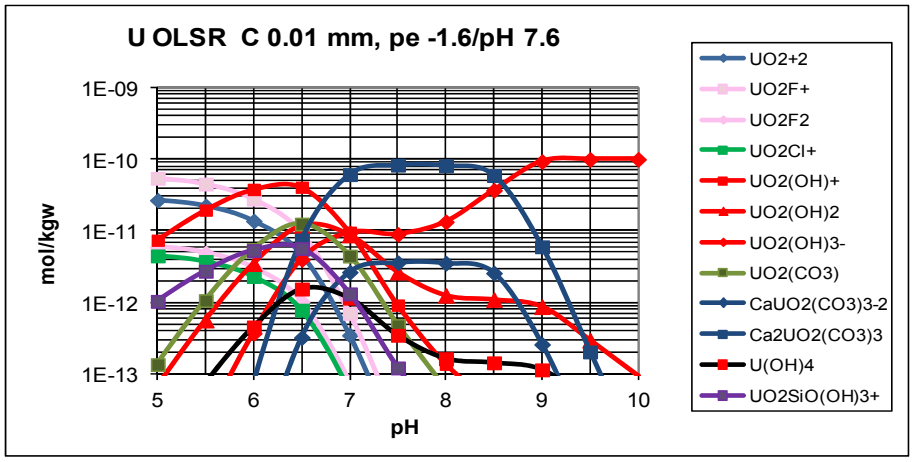

Figure U-9. *Speciation of U in saline OLSR reference water in equilibrium with calcite at pH 7.5 and higher.*

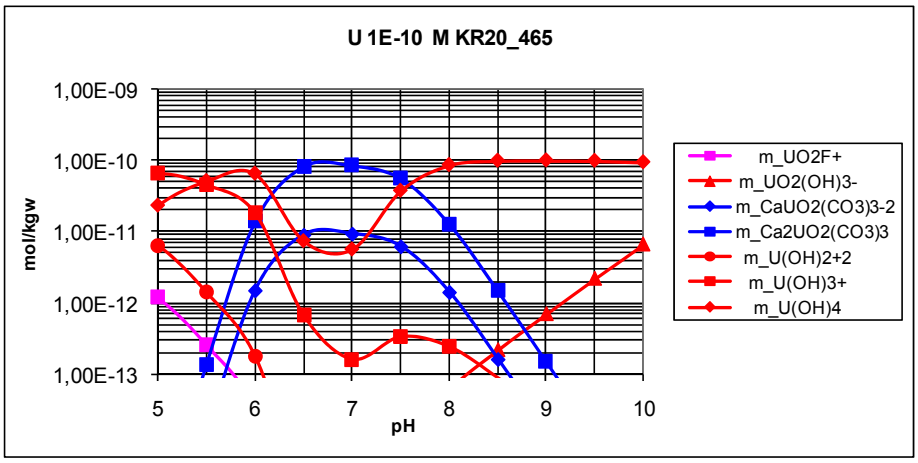

Figure U-10. *Speciation of U in saline groundwater KR20_465_1, pe -4/pH 7.5.*

The speciation of uranium in saline groundwater KR20_465_1 is shown in Figure U-10. In saline groundwater, the contribution of Ca-U(VI)-carbonato complexes decreases. $U(OH)_4$ is the main species at pH higher than 7.6.

23.2 Sorption on rocks

Oxidising and "mildly reducing" conditions

The sorption mechanism of uranyl ion at low pH is cation exchange. Lee et al. (2009) showed that sorption of UO_2^{2+} on biotite was enhanced by high Na^+ or Ca^{2+} back-electrolyte concentration, probably due to the expansion of the biotite structure by exchange of the hydrated Na^+ and Ca^{2+} cations for interlayer K^+ and the penetration of UO_2^{2+} to biotite.

Under low carbonate conditions (glacial meltwater OLGA), the sorption on aluminosilicate minerals at pH > 4 is dominated by $UO_2(OH)^+$ and $UO_2(OH)_2$ complexes, as demonstrated by the comparison of speciation in OLGA and sorption modelling on montmorillonite by Bradbury & Baeyens (2005, 2009). In carbonate-containing solutions, the sorption on montmorillonite is the same as in carbonate-free solutions from pH 4 to pH 7, but sorption decreases with pH owing to the fact that the anionic U(VI)-carbonato complexes are non-sorbing, as shown in Pablan & Turner (1977). Fresh ALLMR(-MO), brackish OLBA and saline OLSO reference waters all contain alkaline-earth cations and carbonate in concentrations such that formation of Ca-uranyl-carbonato complexes takes place. Sorption of U(VI) in calcium and carbonate-containing solutions in near neutral pH was shown to be 2-3 times lower than when $(UO_2)_2CO_3(OH)_3^-$ is the dominant soluble species instead of CaU(VI)-carbonato complexes (Meleshyn et al. 2009, Stewart et al. 2010). In all the groundwaters here concerned, $(UO_2)_2CO_3(OH)_3^-$ is only a minor species.

Reducing conditions

In methanic and low carbonate reducing conditions, the main soluble uranium species in the groundwaters is $U(OH)_4$. No sorption data where the uranium oxidation state is convincingly shown to be solely U(IV) for crystalline rocks exist in the open literature. It has been shown that in redox conditions that are thermodynamically favourable to U(VI) reduction to U(IV), the rate of abiotic reduction of U(VI) to U(IV) by ferrous iron-containing minerals is slow (Hakanen & Lindberg 1995). Sorption under anoxic conditions was determined for crushed Olkiluoto mica gneiss with grain size <0.5 mm. Sorption of U was higher than 99 %. In samples comprising rock slices, U(IV) and Np(IV) in the samples was determined by applying the liquid extraction method. The highest proportion of U(IV) of the total U in the experiments was only 34 %. Most of the U that was removed from solution was U(IV). Only a lower limit of the R_d value of U for the crushed rock was determined, which was 0.6 m^3/kg.

23.2.1 Source data

Sorption of uranium for the selected rocks in the fresh ALLMR and saline OLSR reference waters was determined by the batch method (Methodology described in Appendix 4). The R_d values for the rocks are given in Figures U-11 – U-14. The U(VI)-233 tracer was used. The experiments were carried out under inert atmosphere conditions, but during the experiments U(VI) was not assumed to be reduced to U(IV).

No data for the sorption of U(IV) on rocks or clays enabling estimation of K_d values has come to the attention of the authors. It is assumed that the sorbing species of U(IV) is the $U(OH)_4$ complex.

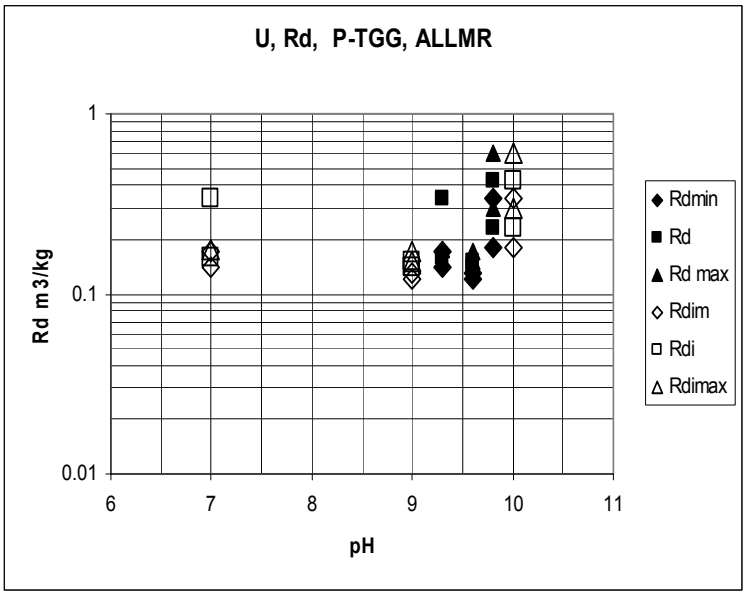

Figure U-11. *R_d values (m^3/kg) of uranium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss in anoxic fresh ALLMR reference water. Open symbols are for initial (i) pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

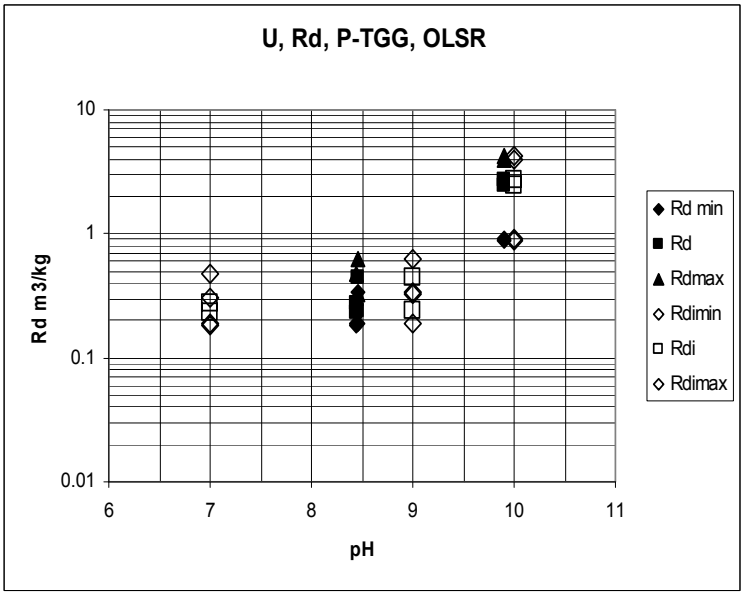

Figure U-12. *R_d values (m^3/kg) of uranium for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss in anoxic saline OLSR reference water. Open symbols are for initial (i) pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

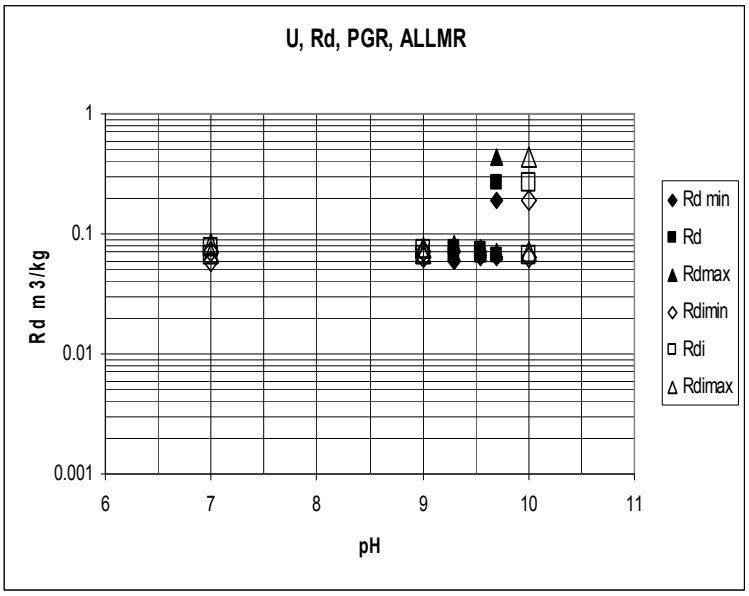

Figure U-13. *R_d values (m^3/kg) of uranium for PGR Olkiluoto pegmatitic granite in anoxic fresh ALLMR reference water. Open symbols are for initial (i) pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

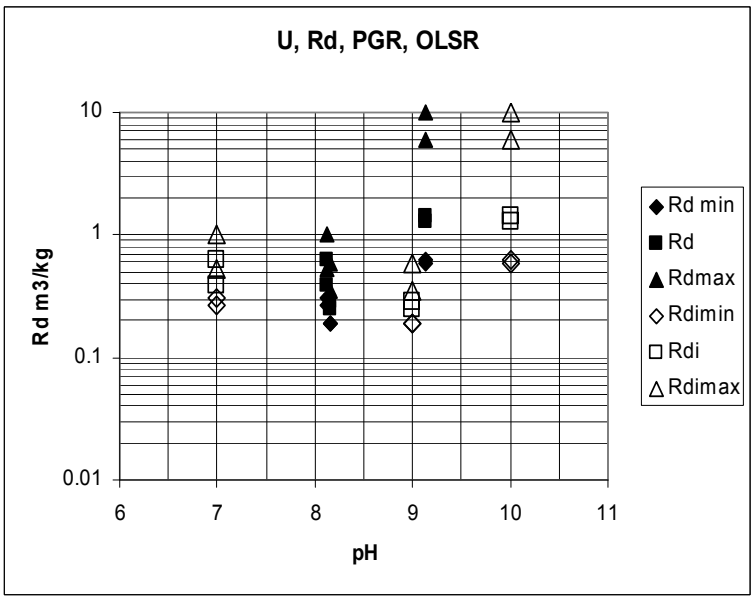

Figure U-14. *R_d values (m^3/kg) of uranium for PGR Olkiluoto pegmatitic in anoxic fresh ALLMR reference water. Open symbols are for initial (i) pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

23.2.2 Best estimate K_d values

The best estimate K_d values for U(VI) were calculated from the R_d values using the ratio of the calculated surface areas of micaceous minerals+hornblende as the conversion

factor. To derive the K_d value for other rocks, it was assumed that in crushed T-TGG all of the surface area of micas+hornblende was accessible to sorption. In the conversion of R_d to K_d for T-TGG, only 50 % of this surface area was assumed accessible. In carbonate-free conditions, the sorption of U(VI) on illite was the same at pH 6-9 and in carbonate (ambient atmosphere) containing solutions, sorption reached a maximum at about pH 6. (Bradbury & Baeyens 2005, 2009). No correction for lower pH of OLGO than in the source data to ALLMR is proposed and the same value is proposed for OLGO as for ALLMR.

The sorbing U(VI) species are probably uranyl hydroxo complexes. The R_d values were almost the same for pH 7-9. An increase of sorption as pH increases to 10 is observed for all rocks and reference waters. Sorption in the carbonate-free OLSR was only marginally higher than in the carbonate-containing fresh ALLMR reference water. The best estimate K_d values in OLGO, ALLMO and OLSO were derived from the lowest R_d values for both rocks and reference water. The experiments were performed only in fresh ALLMR and saline OLSR reference waters, thus ALLMR was chosen to represent the fresh OLGO and ALLMO, and OLSR the saline OLSO reference waters.

Table U-1. *Fraction of $U(OH)_4$ of total uranium in waters and best estimate K_d values (m^3/kg) of U for rocks in the reference waters. Waters KR4 = KR4_81_1; KR20 = KR20_465_1; KR6 = KR6_135_8. Rocks T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

T-MGN							
water	pH	fraction of $U(OH)_4$	K_d (m^3/kg)		pH	fraction of $U(OH)_4$	K_d (m^3/kg)
OLSR	8.3	1	8.0E+00		10	1	8.0E+00
KR20	7.4	0.1	8.0E-01		10	1	8.0E+00
KR6(OLBA)	7.6	0.01	8.0E-02		10	1	8.0E+00
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	3.0E+00		10	1	8.0E+00
P-TGG							
OLSR	8.3	1	4.0E+00		10	1	4.0E+00
KR20	7.4	0.1	4.0E-01		10	1	4.0E+00
KR6(OLBA)	7.6	0.01	4.0E-02		10	1	4.0E+00
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	1.5E+00		10	1	4.0E+00
T-TGG							
OLSR	8.3	1	4.0E+00		10	1	4.0E+00
KR20	7.4	0.1	4.0E-01		10	1	4.0E+00
KR6(OLBA)	7.6	0.01	4.0E-02		10	1	4.0E+00
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	1.0E+00		10	1	4.0E+00
PGR							
OLSR	8.3	1	1.0E+00		10	1	1.0E+00
KR20	7.4	0.1	1.0E-01		10	1	1.0E+00
KR6(OLBA)	7.6	0.01	1.0E-02		10	1	1.0E+00
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	3.0E-01		10	1	1.0E+00

K_d values for the rocks in OLGA, OLBA, OLSR, KR4_81_1 and KR20_465_1 are estimated based on sorption of $U(OH)_4$. The sorption of $Th(OH)_4$ is used as an analogue. The hydrolysis constants of U(IV) are larger than those of Th(IV). Applying the LFER (Linear Free Energy Relationship) theory suggests that sorption of $U(IV)(OH)_4$ is higher than that of $Th(OH)_4$. Using Th as an analogue for U(IV) most probably does not overestimate the sorption of $U(IV)(OH)_4$. The K_d values of U(IV) are estimated to be the same as for Th (see Chapter 20.2.2). In the waters, the sorption of U(IV) is assumed to be the K_d of Th multiplied by the calculated fraction of $U(IV)(OH)_4$ of total U at the pH of the water (Table U-1). The best estimate K_d values for rocks in the waters are given in Tables U-2 – U-5.

Table U-2. *Best estimate K_d values (m^3/kg) of U(IV,VI) for T-MGN Olkiluoto T-series mica gneiss, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.0E+00**	**4.2E-02**	**4.2E-02**	**4.2E-02**	**8.0E-02**	**8.0E+00**	**5.4E-02**	**2.2E-02**	**8.0E-01**
10	8.0E+00	3.2E-02	3.2E-02	3.2E-02	8.0E+00	8.0E+00	5.4E-02	2.2E-02	8.0E+00

Table U-3. *Best estimate K_d values (m^3/kg) of U(IV,VI) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.5E+00**	**2.1E-02**	**2.1E-02**	**2.1E-02**	**4.0E-02**	**4.0E+00**	**3.5E-02**	**1.4E-02**	**4.0E-01**
10	4.0E+00	2.1E-02	2.1E-02	2.1E-02	4.0E+00	4.0E+00	3.5E-02	1.4E-02	4.0E+00

Table U-4. *Best estimate K_d values (m^3/kg) of U(IV,VI) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**1.0E+00**	**6.8E-03**	**6.8E-03**	**6.8E-03**	**4.0E-02**	**4.0E+00**	**2.5E-02**	**4.7E-03**	**4.0E-01**
10	4.0E+00	6.8E-03	6.8E-03	6.8E-03	4.0E+00	4.0E+00	2.5E-02	4.7E-03	4.0E+00

Table U-5. *Best estimate K_d values (m^3/kg) of U(IV,VI) for PGR Olkiluoto pegmatitic granite, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.0E-01**	**2.8E-03**	**2.8E-03**	**2.8E-03**	**1.0E-02**	**1.0E+00**	**1.0E-02**	**1.9E-03**	**1.0E-01**
10	1.0E+00	2.8E-03	2.8E-03	2.8E-03	1.0E+00	1.0E+00	1.0E-02	1.9E-03	1.0E+00

Table U-7. *Fraction of $U(OH)_4$ of total uranium in waters and lower limit K_d values (m^3/kg) of U(IV) for rocks. Waters KR4 = KR4_81_1; KR20 = KR20_465_1; KR6 = KR6_135_8. Rocks T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

T-MGN							
water	pH	fraction of $U(OH)_4$	K_d (m^3/kg)		pH	fraction of $U(OH)_4$	K_d (m^3/kg)
OLSR	8.3	1	1.6E+00		10	1	1.6E+00
KR20	7.4	0.1	1.6E-01		10	1	1.6E+00
KR6(OLBA)	7.6	0.01	1.6E-02		10	1	1.6E+00
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	6.0E-01		10	1	1.6E+00
P-TGG							
OLSR	8.3	1	8.0E-01		10	1	8.0E-01
KR20	7.4	0.1	8.0E-02		10	1	8.0E-01
KR6(OLBA)	7.6	0.01	8.0E-03		10	1	8.0E-01
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	5.0E-02		10	1	8.0E-01
T-TGG							
OLSR	8.3	1	2.0E-01		10	1	2.0E-01
KR20	7.4	0.1	2.0E-02		10	1	2.0E-01
KR6(OLBA)	7.6	0.01	2.0E-03		10	1	2.0E-01
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	5.0E-02		10	1	2.0E-01
PGR							
OLSR	8.3	1	2.0E-02		10	1	2.0E-02
KR20	7.4	0.1	2.0E-03		10	1	2.0E-02
KR6(OLBA)	7.6	0.01	2.0E-05		10	1	2.0E-02
KR4	7.8	<0.001	-		10	< 0.001	-
OLGA	5.8	1	6.0E-03		10	1	2.0E-02

23.2.3 Lower limit K_d values

The lower limit K_d values for U(VI) in ALLMO, OLGO, OLSO and KR4_81_1 waters were calculated from the best estimate K_d values using the uncertainty factor calculated for each rock type. These factors are shown in Table U-6. In cases where the scattering of R_d values is profound, its contribution was taken into account by derivation of the

best estimate K_d values from the lowest R_d values. The scattering was included no further in the uncertainty factors. For T-MGN, the method of deriving K_d from the data for P-TGG is conservative, and the same uncertainty as for P-TGG is used. The lower limit K_d values of U(VI) are shown in Tables U-8 – U-11.

In OLGA, OLBA, OLSR and KR20_465_1 waters, the K_d value of U(IV) is the lower limit K_d of Th multiplied by the calculated fraction of $U(IV)(OH)_4$ of U at the pH of the water (Table U-7) (see Chapter 20.2.3). The calculated lower limit K_d values of U(IV) are shown in Tables U-8 – U-11.

Table U-6. *The uncertainty factors of U for rocks. T-MGN = Olkiluoto T-series mica gneiss; P-TGG = Olkiluoto P-series tonalite granodiorite granite gneiss; T-TGG = Olkiluoto T-series tonalite granodiorite granite gneiss; PGR = Olkiluoto pegmatitic granite.*

Reference rock	Factor for random error calculation
T-MGN, P-TGG	5
T-TGG	20*
PGR	50*
*error propagation using the errors in the mica contents and BET (surface area) of micas and crushed rock yield unrealistically low correction factor value for T-MGN and PGR. Omitting the error in BET of crushed rock, the factor for T-TGG is 7 and for PGR 43.	

Table U-8. *Lower limit K_d values (m^3/kg) of U(IV,VI) for T-MGN Olkiluoto T-series mica gneiss, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-MGN									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**6.0E-01**	**8.4E-03**	**8.4E-03**	**8.4E-03**	**1.6E-02**	**1.6E+00**	**1.1 E-02**	**4.4E-03**	**1.6E-01**
10	1.6E+00	6.4E-03	6.4E-03	6.4E-03	1.6E+00	1.6E+00	1.1E-02	4.4E-03	1.6E+00

Table U-9. *Lower limit K_d values (m^3/kg) of U(IV,VI) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

P-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**3.0E-01**	**4.2E-03**	**4.2E-03**	**4.2E-03**	**8.0E-03**	**8.0E-01**	**7.0E-03**	**2.8E-03**	**8.0E-02**
10	8.0E-01	4.2E-03	4.2E-03	4.2E-03	8.0E-01	8.0E-01	7.0E-03	2.8E-03	8.0E-01

Table U-10. *Lower limit K_d values (m^3/kg) of U(IV,VI) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

T-TGG									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**5.0E-02**	**3.3E-04**	**3.3E-04**	**3.3E-04**	**2.0E-03**	**2.0E-01**	**1.3E-03**	**2.4E-04**	**2.0E-02**
10	2.0E-01	3.3E-04	3.3E-04	3.3E-04	2.0E-01	2.0E-01	1.3E-03	2.4E-04	2.0E-01

Table U-11. *Lower limit K_d values (m^3/kg) of U(IV,VI) for PGR Olkiluoto pegmatitic granite, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

PGR									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**6.0E-03**	**5.6E-05**	**5.6E-05**	**5.6E-05**	**2.0E-4**	**2.0E-02**	**2.0E-04**	**3.8E-05**	**2.0E-03**
10	2.0E-02	5.6E-05	5.6E-05	5.6E-05	2.0E-02	2.0E-02	2.0E-04	3.8E-05	2.0E-02

23.3 Sorption on clays

Amayri et al. (2004) wrote that sorption of uranium on KGa-1b kaolinite (4g/L) in CO_2-free solution was 100 % at pH 6-10, whereas sorption under atmospheric conditions decreased from 100 % at pH 6 to 0 % at pH 10.5. High sorption (log R_d 4.8 mL/g) on illite (Bradbury & Baeyens 2009) and montmorillonite (log R_d 5.2 mL/g) (Bradbury & Baeyens 2005) in CO_2-free $NaClO_4$ solution was measured. The maximum sorption was at pH 6 to both clays. Under conditions open to atmospheric CO_2, the sorption decreased from the maximum to nearly zero at pH 9. This is in accordance with that the anionic U(VI) carbonato complexes being low- or non-sorbing. No data for the sorption of U(IV) have come to the attention of the authors.

23.3.1 Source data

Sorption of U(VI) was determined by the batch method for KGa-1b kaolinite and IMt-1 illite in fresh ALLMR and saline OLSR reference waters (Methodology described in Appendix 4). The R_d values are indicated in Figures U-15 to U-18 for the initial pH and final pH of the solution.

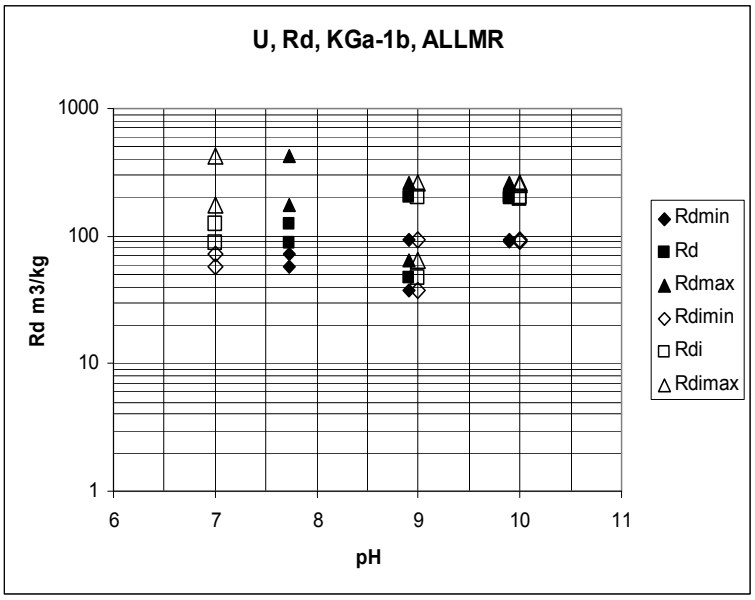

Figure U-15. *R_d values (m^3/kg) of uranium for kaolinite KGa-1b in anoxic fresh ALLMR reference water. Open symbols are for initial (i) pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

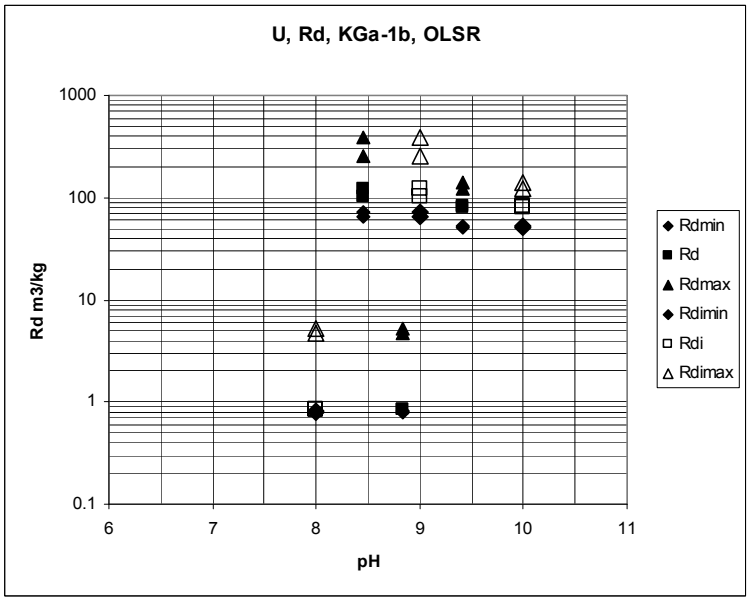

Figure U-16. *R_d values (m^3/kg) of uranium for kaolinite KGa-1b in anoxic saline OLSR reference water. Open symbols are for initial (i) pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

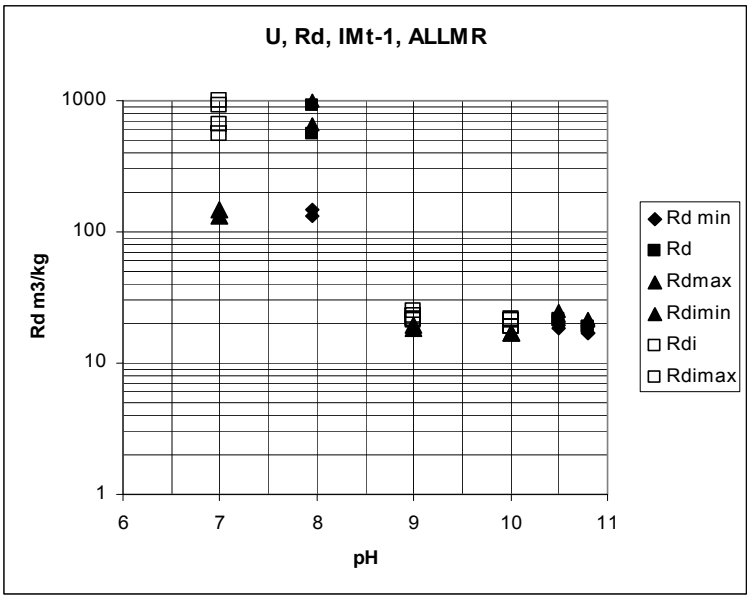

Figure U-17. *R_d values (m^3/kg) of uranium for illite IMt-1 in anoxic fresh ALLMR reference water. Open symbols are for initial pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

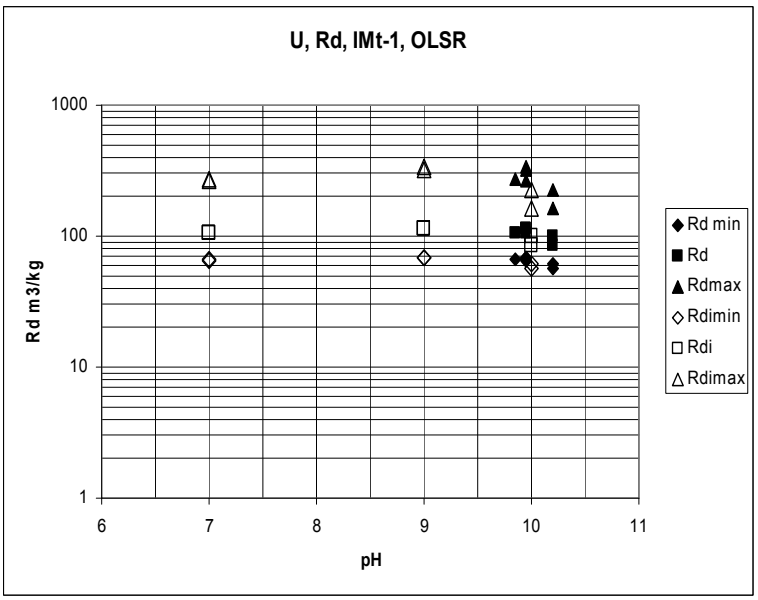

Figure U-18. *R_d values (m^3/kg) of uranium for illite IMt-1 in anoxic saline OLSR reference water. Open symbols are for initial pH. The maximum (max) and minimum (min) values are based on 1σ counting error.*

23.3.2 Best estimate K_d values

The K_d values were calculated from the lowest values of R_d values for clays and reference water. There was a strong sorption to illite at pH 7–8. These R_d values were

taken as representative R_d values at pH 6–10, supported by sorption on the rocks that indicated the same or higher sorption at pH higher than 8. The R_d values at pH 9–11 in ALLMR are low, most probably due to experimental difficulties. The same is assumed for low R_d values at pH 8 and 8.7 for kaolinite in OLSR. These are omitted in the estimation of the R_d values for the clays.

Experimental results in oxic conditions are not available: the sorption in anoxic and oxic conditions was taken to be the same for U(VI), the carbonate concentration being more decisive. The experiments were performed only in fresh ALLMR and saline OLSR reference waters, thus ALLMR was chosen to represent the fresh ALLMO, and OLSR the saline OLSO reference waters. For glacial meltwater OLGO, the R_d values of ALLMR were used without carbonate correction.

Since no sorption data for U(IV) were available, Th(IV) was used as an analogue for estimation of the best estimate values (see Chapter 20.3.2). The K_d values in OLGA, OLBA, OLSR and KR20_465_1 waters are calculated from values for Th by multiplying the K_d values of Th by the fraction of $U(OH)_4$ of total uranium in the waters (Table U- 1). The best estimates of K_d of U for clays are shown in Tables U-12 – U13.

23.3.3 Lower limit K_d values

The overall uncertainty factor (UF_{tot}) for intact fracture clays at Olkiluoto is calculated from the individual uncertainty factors for each error-producing step. The overall error for clays is obtained by multiplying the error parameters:

Table U-12. *Best estimate K_d values (m^3/kg) of U(IV,VI) for kaolinite at Olkiluoto, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**6.0E+01**	**4.7E+01**	**4.7E+01**	**4.7E+01**	**3.2E+01**	**7.2E+01**	**7.2E+01**	**3.2E+01**	**7.2E+01**
10	2.0E+02	4.7E+01	4.7E+01	4.7E+01	3.2E+01	7.2E+01	7.2E+01	3.2E+01	7.2E+01

Table U-13. *Best estimate K_d values (m^3/kg) of U(IV,VI) for illite at Olkiluoto, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.0E+01**	**1.9E+01**	**1.9E+01**	**1.9E+01**	**1.3E+01**	**8.4E+01**	**8.4E+01**	**1.3E+01**	**8.4E+01**
10	2.0E+01	1.9E+01	1.9E+01	1.9E+01	1.3E+01	8.4E+01	8.4E+01	1.3E+01	8.4E+01

$$UF_{tot} = UF_{source} * UF_{model} * UF_{CEC} * UF_{spec} * UF_{pH} * UF_{lab\_field} \quad \text{(U-1)}$$

The lower limit of the K_d(LL) value is obtained by dividing each best estimate K_d(BE) value by its overall uncertainty factor UF_{tot}:

$$K_d\,(LL) = K_d(BE)/UF_{tot} \quad \text{(U-2)}$$

Since no sorption data for U(IV) were available, Th(IV) was used as an analogue for the best estimate values in waters where all or part of the uranium is in the U(IV) form (see Chapter 20.3.3). Since even a small amount of U(IV) increases the K_d value and the contribution of (VI) would be negligible, the lower limit values are taken to be the same as Th(IV) multiplied by the fraction of $U(OH)_4$ of the total uranium.

Kaolinite

UF_{source} varies from 1.27 to 1.41. One sigma deviation in R_d values at the lowest R_d value is included in the uncertainty factor UF_{source}.

UF_{model} = 1. No model was used.

UF_{CEC} = 1. The sorption mechanism is ion exchange. At high pH, the impact of sorption by surface complexation is not taken into account. Since the source data were performed in well-crystallised kaolinite, there is no need for a correction factor concerning differences between the source data and the reference conditions. Well-crystallised kaolinite sorbs in equal amounts or less compared with the Olkiluoto kaolinite (the state of crystallinity is unknown). However, the CEC for kaolinite is in general not very high and it was considered that the uncertainty is not significant (see Chapter 3).

UF_{spec} = 1.4. Difference in speciation is expected between the reference waters due to complexation, especially the contribution of U(IV). The same K_d values cannot be used for all waters when the K_d values are calculated from other reference waters and from Th(IV) analogue approach.

UF_{pH} = 1. No pH dependency at the pH region considered.

UF_{lab_field} = 2. Upscaling from laboratory data to whole clay matrix is covered by the factor 2.

UF_{tot} varies from 2.5 to 4.

The uncertainty factors of U(VI) are collected in Table U-14. Only those factors which are greater than one are listed. Also, if the correction factors are the same for reference pH and pH 10, only one is reported.

The lower limit K_d values of U for kaolinite in the Olkiluoto geosphere are calculated in Table U-16.

Illite

For illite at Olkiluoto, the uncertainty factors are almost the same as for kaolinite.

UF_{CEC} = 1.3. There is an uncertainty in the CEC values of the IMt-1 illite compared with the Olkiluoto site illite.

UF_{tot} varies from 4 to 5.5.

The uncertainty factors of U(VI) are collected in Table U-15. Only those factors which are greater than one are listed. Also, if the correction factors are the same for reference pH and pH 10, only one is reported.

The lower limit K_d values of U for illite at Olkiluoto are calculated in Table U-17.

Table U-14. *The uncertainty factors (UF) of U(VI) for kaolinite Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	UF_{source}	UF_{spec}	$UF_{Lab\ field}$	UF_{tot}
OLGO	1.3	1.4	2	3.6
ALLMR	1.3	1	2	2.5
ALLMO	1.3	1.4	2	3.6
OLSO	1.4	1.4	2	4
KR4	1.3	1.4	2	3.6

Table U-15. *The uncertainty factors (UF) of U(VI) for illite Olkiluoto. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Water	UF_{source}	UF_{CEC}	UF_{spec}	$UF_{Lab\ field}$	UF_{tot}
OLGO	1.1	1.3	1.4	2	4
ALLMR	1.1	1.3	1	2	2.9
ALLMO	1.1	1.3	1.4	2	4
OLSO	1.5	1.3	1.4	2	5.5
KR4	1.1	1.3	1.4	2	4

Table U-16. *Lower limit K_d values (m^3/kg) of U(IV,VI) for kaolinite at Olkiluoto, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**2.0E+01**	**1.3E+01**	**1.9E+01**	**1.3E+01**	**2.7E+00**	**1.1E+01**	**1.8E+01**	**9.0E+00**	**2.2E+01**
10	8.4E+01	1.3E+01	1.9E+01	1.3E+01	3.8E+01	1.1E+01	1.8E+01	9.0E+00	2.2E+01

Table U-17. *Lower limit K_d values (m^3/kg) of U(IV,VI) for illite at Olkiluoto, in conditions where no reduction of U(VI) is assumed (OLGO, ALLMR, ALLMO, OLSO and KR4_81_1) and for the waters (OLGA, OLBA, OLSR and KR20_465_1) where all or part of U is at oxidation state U(IV), at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite									
pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
REF	**7.5E+00**	**4.7E+00**	**6.4E+00**	**4.7E+00**	**4.9E+00**	**3.1E+01**	**1.5E+01**	**3.3E+00**	**3.1E+01**
10	7.5E+00	4.7E+00	6.4E+00	4.7E+00	4.9E+00	3.1E+01	1.5E+01	3.3E+00	3.1E+01

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24 PLUTONIUM

24.1 Speciation

Plutonium may exist in environmental waters at oxidation states Pu(III), Pu(IV), Pu(V) and Pu(VI). Solubility limits of Pu have been calculated by Grive et al. (2008) for the reference groundwaters in the KBS-3H deposition concept using the updated data base of Duro et al. (2005). The solubility limits ranged from $1.5 \cdot 10^{-10}$ M in dilute brackish KR6_58_1 water to $8 \cdot 10^{-9}$ M in brackish saline KR20_465_1 water. Speciation in the reference waters in this report was calculated with the PHREEQC programme to Pu-concentration of $1 \cdot 10^{-10}$ M using the Thermo_Chimie Version 7b database (ANDRA 2009).

Saline waters

In addition to the reference waters, speciation of Pu was calculated for the solution conditions of the brackish/saline OLKR5 groundwater used in sorption studies of Pu for Olkiluoto rocks (Kulmala et al. 1998). In reducing conditions, $Pu(III)^{3+}$, $Pu(III)OH^{2+}$, $Pu(III)Cl_2^{+}$, $Pu(III)(CO_3)^{+}$ and $Pu(IV)(OH)_4$ contribute to the speciation (Figures Pu-1, Pu-2). The measured pH/E_h values in OLKR5 water in Kulmala et al. (1998) fall to a pe/pH range where both Pu(III) and Pu(IV) species can exist at the same time.

The OLSR reference water is more saline than OLKR5 and the carbonate concentration is lower than in OLKR5. For redox conditions (pe-4/pH7.5), the Pu^{3+} and $Pu(III)Cl^{2+}$ concentrations are equal and the impact of $Pu(III)(CO_3)^{+}$ lower than in OLKR5 water. The speciation of Pu in saline Olkiluoto KR20_465_1 groundwater is given in Figure Pu-3. The higher chloride salinity in the brackish/saline OLKR5 water is followed by the result that at pH lower than pH 8, the fraction of Pu(III) chlorido complex in OLKR5 water is higher and the fraction of Pu^{3+} lower than in KR20_465_1 water. The higher carbonate concentration in KR20_465_1 is followed by the result that in the pH of this water (around pH 7.4), the Pu(III) carbonato complexes are more abundant than in OLKR5 water.

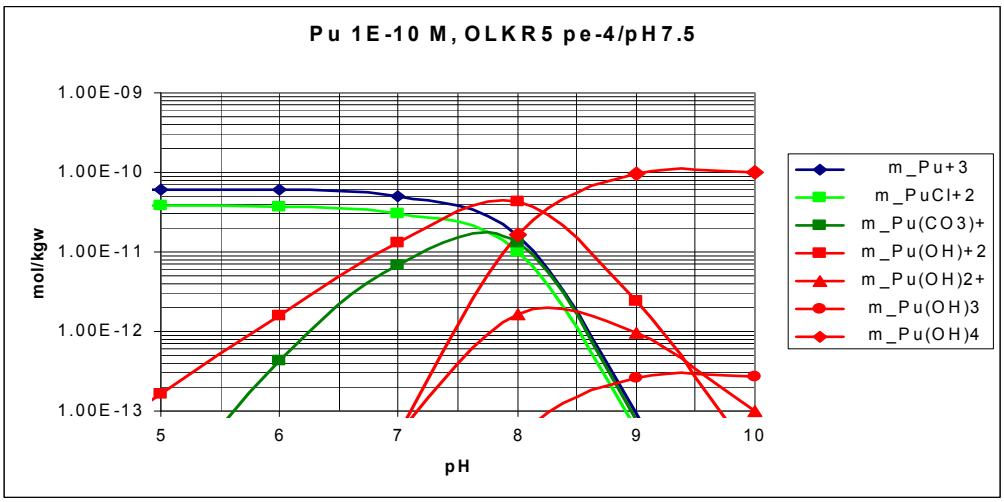

Figure Pu-1. *Speciation of plutonium in brackish/saline OLKR5 groundwater, pe -4.0 at pH 7.5.*

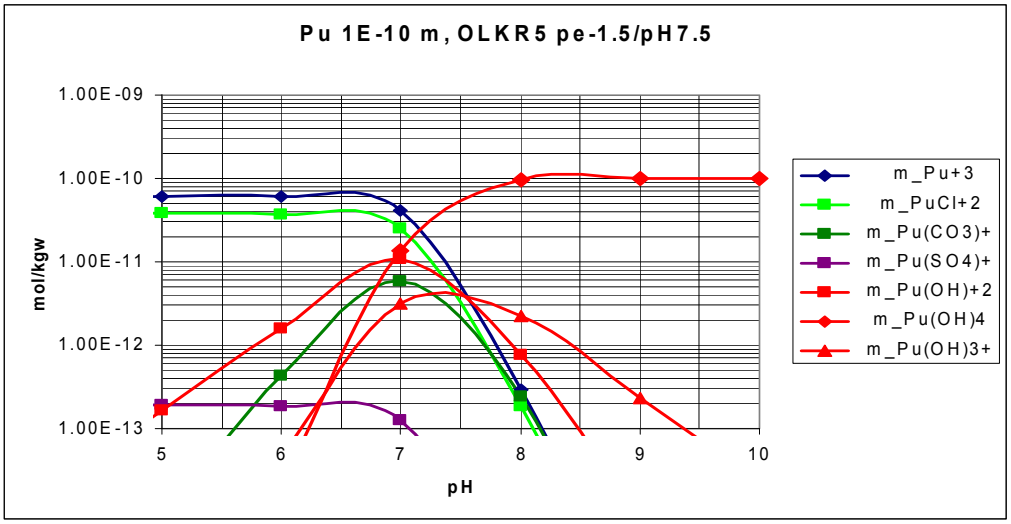

Figure Pu-2. *Speciation of plutonium in brackish/saline OLKR5 groundwater, pe -1.5 at pH 7.5.*

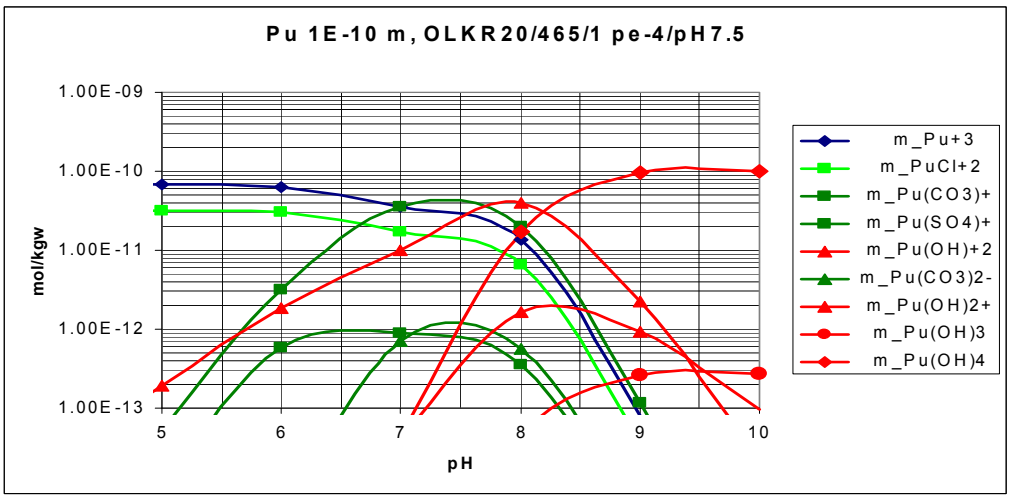

Figure Pu-3. *Speciation of plutonium in saline Olkiluoto KR20_465_1 groundwater, pe -4 at pH 7.5.*

At higher than the nominal pH the water becomes oversaturated with respect to calcite. In the modelling, calcite was allowed to precipitate. Speciation in less reducing KR20_465_1 is the same as in OLKR5 (Figure Pu-3). $Pu(IV)(OH)_4$ in these waters is the main species at pH 7.2 and higher. At the pe -4 /pH 7.5 of KR20_465_1 water, the proportion of the Pu(III) species that are assumed to be sorbing (Pu^{3+} and $Pu(OH)^{2+}$) together is about 50 % and the proportion of $Pu(IV)(OH)_4$ is about 1 % of the total Pu. At pH 10 around100 % of Pu is $Pu(OH)_4$.

Brackish waters

The speciation of Pu in the brackish KR6_135_8 water is given in Figure Pu-4. The carbonate concentration of this water is relatively high and increase of pH to higher than the nominal pH is followed by oversaturation of the water with respect to calcite. Hence, the speciation at higher pH is calculated for the water allowing calcite precipitation. Under reducing conditions, the dominant species at pH 7–8.2 is the $Pu(III)(CO_3)^+$ complex. At pH 7.6 of KR6_135_8 and its simulant OLBA water, the proportion of the potentially sorbing species Pu^{3+} and $Pu(III)(OH)^{2+}$ is 35 % together. Only 1 % of Pu is as $Pu(IV)(OH)_4$. At pH 8.2 and higher, the main species is $Pu(OH)_4$. At pH 10, 100 % of Pu is $Pu(OH)_4$. Under less reducing conditions (pe -1.5/pH 7.5), $Pu(IV)(OH)_4$ is the dominant species for the pH range 7.8-10. At pH 7.6 its proportion is about 30 %. The relatively high Ca and Mg concentrations keep the carbonate concentration at such a low level that the impact of Pu(IV) hydroxocarbonato complexes is small.

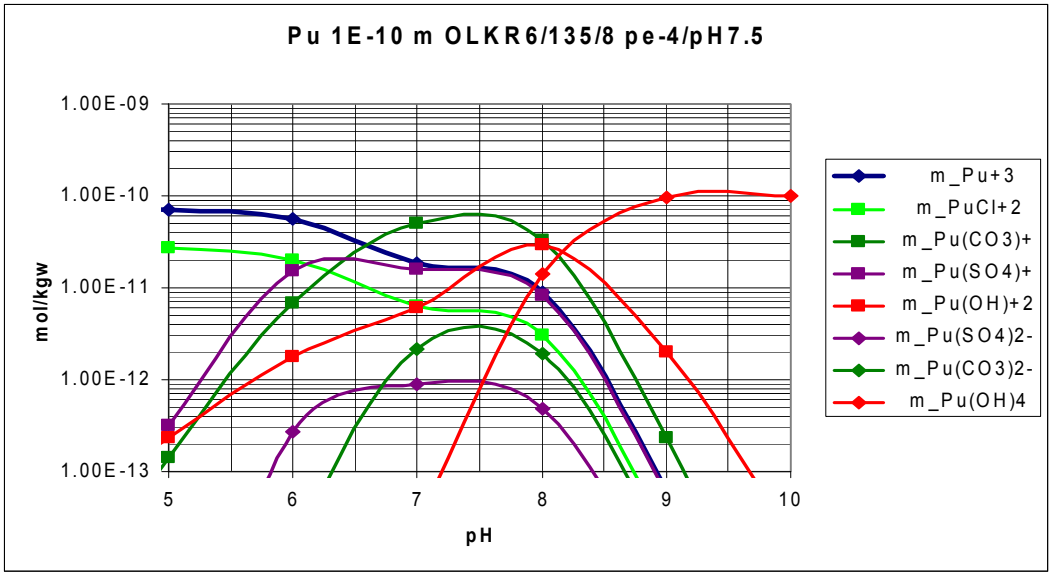

Figure Pu-4. *Speciation of plutonium in the brackish KR6_135_8 groundwater, pe -4.0 at pH 7.5.*

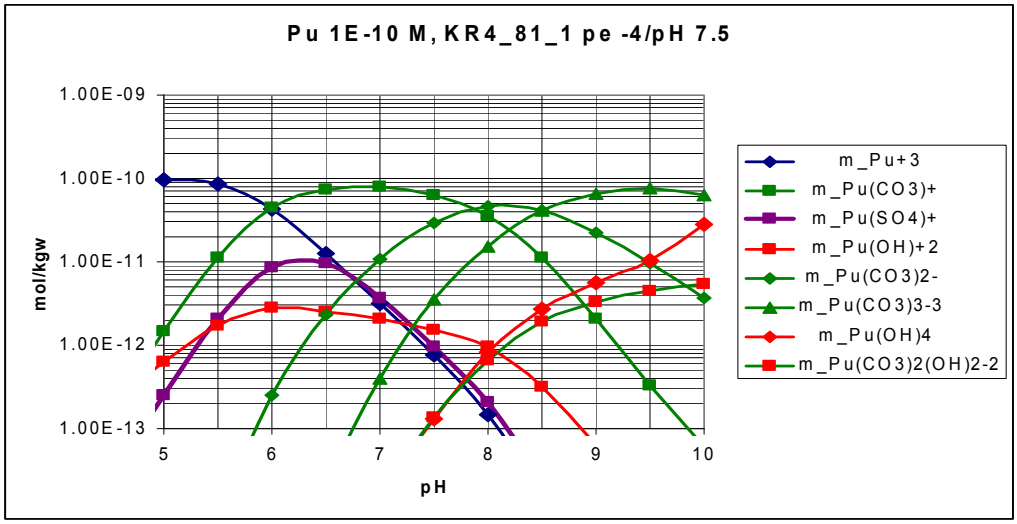

Figure Pu-5. *Speciation of plutonium in brackish Olkiluoto KR4_81_1ground water, pe -4.0 at pH 7.5.*

In the brackish water KR4_81_1, the Pu(III) carbonato complexes are the most abundant (Figure Pu-5). Hydroxo complexes of Pu(III) and Pu(IV) are minor species. The Pu(III) carbonato complexes are also the main species at high pH. At pH 7.8 of this water, the proportion of Pu^{3+}, $Pu(III)(OH)^{2+}$ and $Pu(IV)(OH)_4$ is together only about 2 %. At pH 10, $Pu(OH)_4$ is 30 % of total Pu.

Fresh waters

In the low-salinity groundwaters of Kivetty and Romuvaara used in Kulmala et al. (1998), the carbonate concentration was about 1 mM and the speciation of Pu is about the same as in the fresh ALLMR water (Figure Pu-6). Speciation at pe-4/pH 7.5 is about the same as in KR20_465_1 water. Pu^{3+} and $Pu(III)(OH)^{2+}$ together are 40 % and $Pu(IV)(OH)_4$ is 10 % of total Pu.

Glacial melt waters

In the glacial melt water OLGA in reducing (pe -2.5/ pH 6) and at pe 0/pH 6 conditions, Pu^{3+} is the main species, and at pH 10 the main species is $Pu(IV)(OH)_4$ (Figure Pu-7). In the high-pH Grimsel melt water (pH 9.6), $Pu(IV)(OH)_4$ is the main species at pH 10.

Aerobic waters

Under aerobic conditions in the fresh ALLMO water and in the glacial melt water OLGO, the dominant Pu oxidation state changes with increase of pe and carbonate concentration from Pu(III, IV) (Figure Pu-8) to Pu(IV) and to Pu(V,VI) (Figure Pu-9). In low carbonate glacial OLGO water at high pH, the contribution of $Pu(IV)(OH)_4$ increases from 40 % at pH 9.5 to 60 % at pH 10. In equilibrium with the ambient atmosphere, the higher oxidation states become the main species in OLGO (Figure Pu-10). In oxidising conditions in ALLMO water (Figure Pu-11), the $Pu(V)O_2^+$ ion and the Pu(VI) carbonate complexes become the main species and the impact of $Pu(OH)_4$ is less than 1 %.

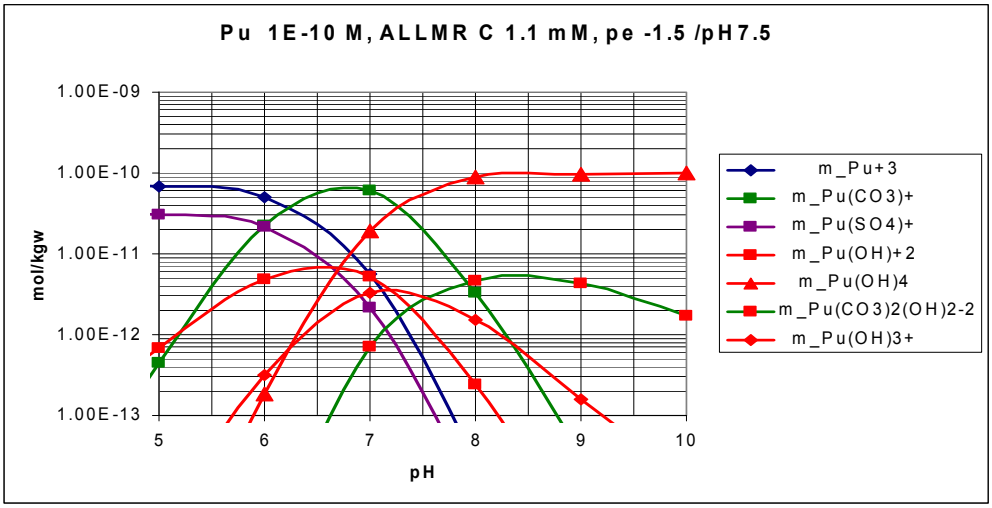

Figure Pu-6. *Speciation of plutonium in fresh ALLMR reference water, pe -1.5 at pH 7.5.*

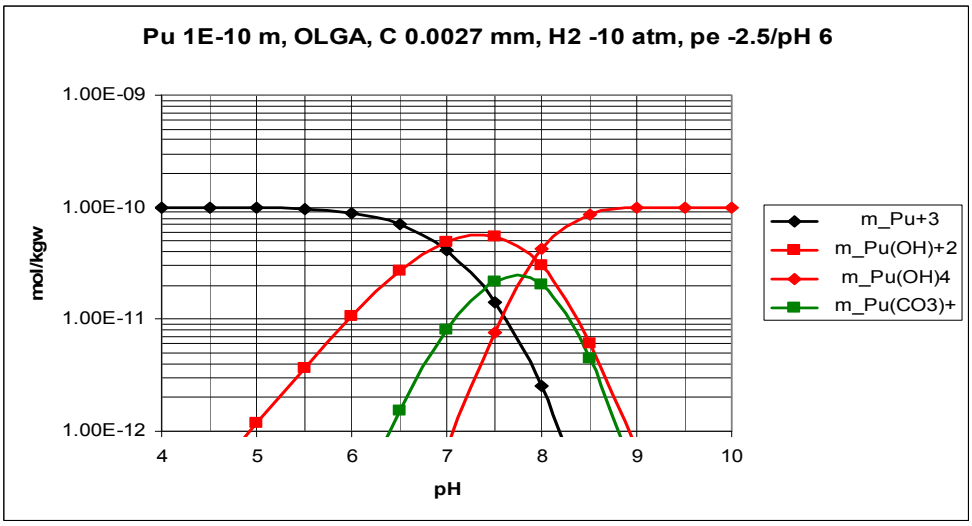

Figure Pu-7. *Speciation of plutonium in the glacial melt water OLGA, pe -2.5 at pH 6.*

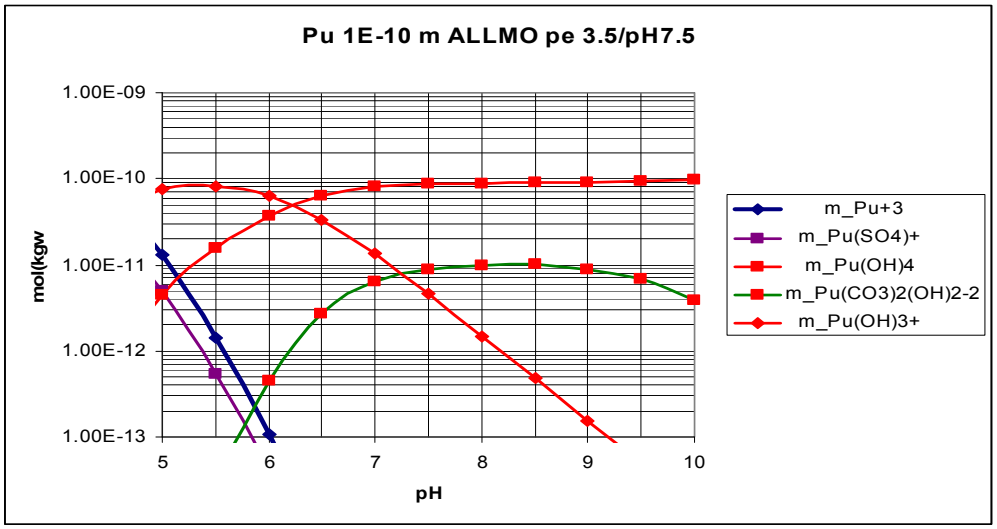

Figure Pu-8. *Speciation of plutonium in fresh ALLMO reference water, pe 3.5/pH 7.5.*

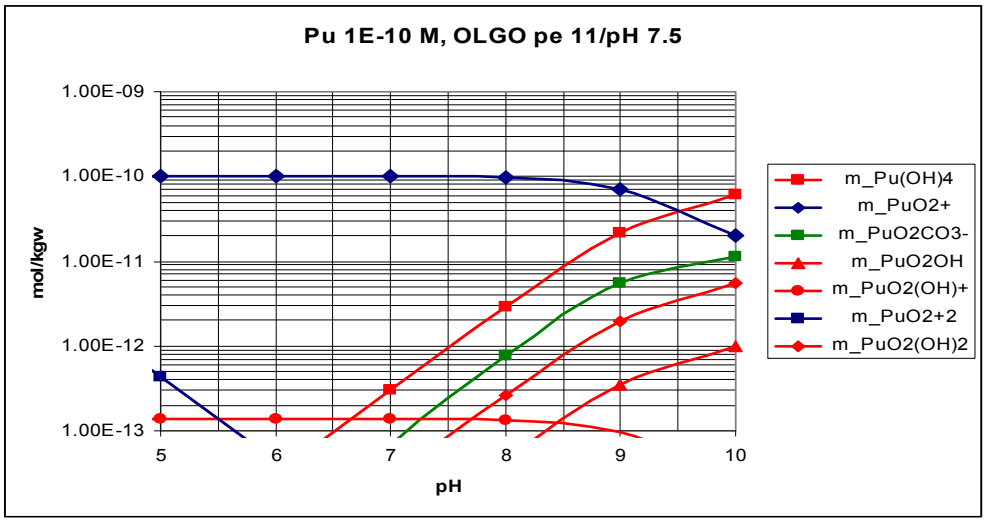

Figure Pu-9. *Speciation of plutonium in aerobic glacial melt water OLGO, pe 11/pH 7.5.*

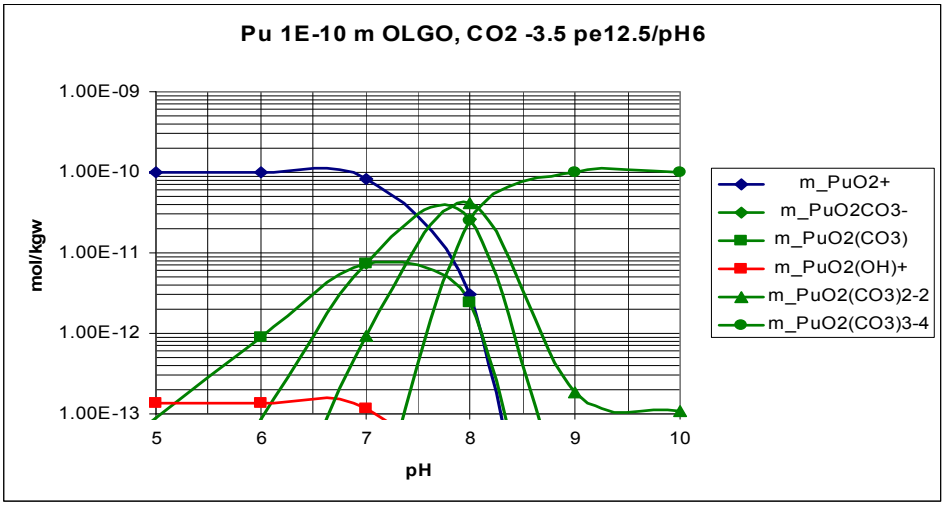

Figure Pu-10. *Speciation of plutonium in oxidising glacial melt water OLGO in equilibrium with atmospheric carbon dioxide, pe 12.5/pH 6.*

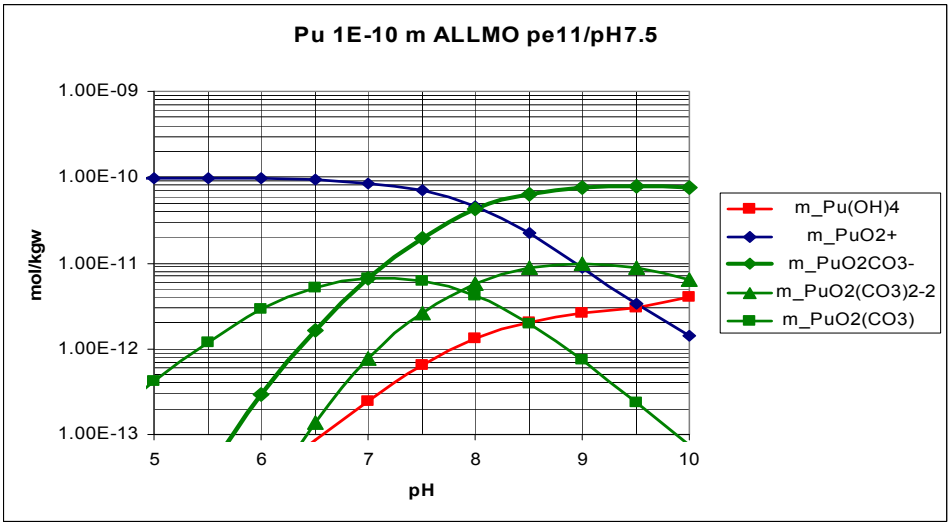

Figure Pu-11. *Speciation of plutonium in oxidising aerobic ALLMO water, pe 11/pH 7.5.*

24.2 Sorption on rocks in reducing (anaerobic) conditions

24.2.1 Source data

Sorption of Pu on Olkiluoto (OL), Kivetty (Ki) and Romuvaara (Ro) rocks in natural groundwaters collected at these Posiva investigation areas was presented in Kulmala et al. (1998). In the experiments, the Pu-236 ($T_{1/2}$ = 2.86 a) isotope was used as the tracer. Sorption in anaerobic conditions on crushed mica gneiss (OLMG), tonalites (OLTON) and granites (OLGR) was given in Tables 5, 6 and 7 in Kulmala et al. (1998). It is noteworthy that the largest R_d values were measured for OL rocks in OLKR5

groundwater under initially aerobic conditions (Kulmala et al. (1998), Appendix C: Table 2). In these samples, the redox conditions were favourable for the $Pu(IV)(OH)_4$ to be the main solution species.

In anaerobic conditions, the R_d values for groundwater-rock combinations from Olkiluoto, Romuvaara and Kivetty had a range of 0.8 m^3/kg to 16 m^3/kg (Kulmala et al. 1998). The larger R_d values were associated with higher redox potential (less reducing conditions). For Romuvaara (Ro) tonalite in the site-specific groundwaters, the R_d values in anaerobic conditions had a range of 0.4 m^3/kg to 9.1 m^3/kg and for Kivetty granite 1.0 to 5.9 m^3/kg. The values were lower than for the Olkiluoto rocks.

The total carbonate concentration in the waters from Romuvaara and Kivetty was about 1 mM. It follows that the speciation of Pu in these waters was near to that in the fresh ALLMR water. As in OLKR5 water, the larger R_d values were associated with higher E_h values (less reducing conditions). Speciation of Pu in OLKR5 in Figures Pu-1 and Pu-2 suggests that in the experimental conditions of Kulmala et al. (1998), Pu(III) and Pu(IV) species both contributed to sorption. In the more reducing E_h/pH conditions, the proportion of Pu(III) is higher, and in less reducing conditions, the proportion of hydroxo complexes of Pu(IV) are more abundant.

The results in Kulmala et al. (1998) indicate high sorption of Pu in anaerobic groundwater conditions. Interpretation and modelling of sorption experiments of plutonium in Kulmala et al. (1998) are difficult, owing to the probable coexistence of more than one oxidation state of plutonium in the system. Guidance on the estimation of sorption of Pu(III) and Pu(IV) is obtained from the sorption behaviour of the more stable oxidation state actinides and lanthanides, Am(III)/Eu(III) for Pu(III), Th(IV) for Pu(IV), Np(V) and U(VI) for Pu(V) and Pu(VI), respectively. In this report, too, sorption results for these analogues are applied to estimate sorption of Pu in a certain oxidation state.

There are no results for sorption of Pu(III) on crystalline rocks. Sorption of Pu(III) on kaolinite in electrolyte solutions at pH 5 to pH 10 was shown to be the same as sorption of Am(III) (Buda et al. 2008). Sorption of Eu(III) on kaolinite was also almost the same as that of Am in Puukko & Hakanen (2001). This supports the estimation that sorption of Pu(III) is the same as that of Eu (III) and Am(III).

24.2.2 Best estimate K_d values for Pu(III)

There are more uncertainties in the effects of solution speciation on sorption of Pu(III) than on sorption of Eu, for which experimental values are also available. According to the LFER approach (Dzombak & Morel 1990, Bradbury & Baeyens 2005) the sorption affinity on ferric hydroxide and on clay minerals is higher for a hydrolysed cation with larger hydrolysis constants. The first hydrolysis constant of Pu(III) is larger than that of Eu (ANDRA 2009, Duro et al. 2005) and sorption of hydroxo complexes of Pu (III) are assumed to be higher than those of Eu. This further entitles the authors to use the same best estimate K_d values and lower limit values for Pu(III) as for Eu and Am. In addition, at low pH (OLGA), the impact of sorption by cation exchange is the same for Eu and Am (Bradbury & Baeyens 2005).

Speciation calculations using the database of Grive et al. (2008) and Thermo_Chimie 7b (ANDRA 2009) indicate that there is a difference in the calculated speciation between Pu(III) and Am(III), especially in low-carbonate conditions. Am(III) and Eu(III) in fresh ALLMR and saline OLSR waters are partly in the form of a cationic silicato-hydroxo complex (see Chapter 19). The impacts of the silicato-hydroxo complexes on sorption are not clear, as the sorption pH edges of Eu and Am (Bradbury & Baeyens 2005) were in agreement and sorption was modelled using only hydroxo complexes, even when the experimental water in sorption experiments of Eu also contained silicates (Poinssot et al. 1999). The databases do not include Pu(III) silicate complexation. In this report, the authors make the assumption that Pu(III) forms the same complexes as Eu and Am.

The R_d values of Eu on the Olkiluoto mica gneiss and granodiorite in ALLMR and OLSR type waters (see sorption of americium Chapter 19) are applied for the derivation of the K_d values of Pu(III) for the reference rocks. The saline, brackish and fresh reference groundwaters have higher carbonate concentration than the non-carbonate ALLMR to which sorption of Eu was determined. The speciation of Pu(III) in reducing conditions in the groundwaters suggests that the main species is the carbonato complex $Pu(III)CO_3^+$, as for Eu when silicate complexation is not taken into account. The sorption of Pu (III) in the Olkiluoto bedrock is taken to be the same as that of Eu. The K_d values of Pu(III) for the rocks are given in Tables Pu-1 – Pu-4. At the reference pH in ALLMR and OLSR, the main oxidation state is Pu(IV) and the K_d values in Tables Pu-10 and Pu-13 are proposed. At pH10, the sorption is due to Pu(IV) only or Pu (IV) and Pu(III) in all waters. In all waters at pH 10, Pu(IV) is estimated to be the sorption determining oxidation state and the Kd values in Tables Pu-10 and Pu-13 are proposed.

Table Pu-1. *The best estimate K_d (m^3/kg) values of Pu(III) for T-MGN Olkiluoto mica gneiss in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-01**	**2.4E+00**	**3.0E+00**	**3.0E+00**	**3.0E+00**	**3.0E+00**
10	3.0E+00	2.7E+00	2.7E+00	2.7E+00	4.5E-02	2.7E+00

Table Pu-2. *The best estimate K_d (m^3/kg) values of Pu(III) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.0E-02**	**9.0E-01**	**1.1E+00**	**1.1E+00**	**1.1E+00**	**1.1E+00**
10	1.1E+00	1.0E+00	1.0E+00	1.0E+00	1.5E-02	1.0E+00

Table Pu-3. *The best estimate K_d (m^3/kg) values of Pu(III) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.0E-02**	**5.0E-01**	**5.8E-01**	**5.8E-01**	**5.8E-01**	**5.8E-01**
10	6.0E-01	5.0E-01	5.0E-01	5.0E-01	8.0E-03	5.0E-01

Table Pu-4. *The best estimate K_d (m^3/kg) values of Pu(III) for PGR Olkiluoto pegmatitic granite in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E-03**	**9.0E-02**	**1.1E-01**	**1.1E-01**	**1.1E-01**	**1.1E-01**
10	1.0E-01	1.0E-01	1.0E-01	1.0E-01	1.5E-03	1.0E-01

24.2.3 Lower limit K_d values for Pu(III)

The same lower limit K_d values as for Eu are suggested. The uncertainties in the estimation of K_d values originate from mineralogical uncertainties and from the strong pH dependence (see Sorption of americium, Chapter 19) in sorption at the pH region of interest for the reducing waters at pH 6-8. Differences in the modelled speciation of Pu(III) and Eu suggest that sorption of Pu(III) most probably is not lower than of Eu, and no additional uncertainty due to use of chemical analogue is regarded necessary. The lower limit K_d values of Pu(III) for the rocks are given in Tables Pu-5 – Pu-8.

Table Pu-5. *The lower limit K_d (m^3/kg) values of Pu(III) for T-MGN Olkiluoto mica gneiss in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-MGN						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E-03**	**1.2E-01**	**1.5E-01**	**1.5E-01**	**1.5E-01**	**1.5E-01**
10	1.5E-01	1.4E-01	1.4E-01	1.4E-01	2.3E-03	1.4E-01

Table Pu-6. *The lower limit K_d (m^3/kg) values of Pu(III) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

P-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**3.5E-03**	**4.5E-02**	**5.5E-02**	**5.5E-02**	**5.5E-02**	**5.5E-02**
10	5.5E-02	5.0E-02	5.0E-02	5.0E-02	7.5E-04	5.0E-02

Table Pu-7. *The lower limit K_d (m^3/kg) values of Pu(III) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

T-TGG						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.5E-03**	**2.5E-02**	**2.9E-02**	**2.9E-02**	**2.9E-02**	**2.9E-02**
10	3.0E-02	2.5E-02	2.5E-02	2.5E-02	4.0E-04	2.5E-02

Table Pu-8. *The lower limit K_d (m^3/kg) values of Pu(III) for PGR Olkiluoto pegmatitic granite in reference waters. The K_d value in bold text is the value at the pH of the reference water. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

PGR						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.2E-04**	**1.8E-03**	**2.2E-03**	**2.2E-03**	**2.2E-03**	**2.2E-03**
10	2.0E-03	2.0E-03	2.0E-03	2.0E-03	3.0E-05	2.0E-03

24.2.4 Best estimate K_d values of Pu in conditions where Pu(IV) is the main oxidation state

Under mildly reducing to mildly oxidising conditions, $Pu(IV)(OH)_4$ and $Pu(IV)(OH)_3^+$ are the main species also in the low-pH region of the groundwaters. Anionic Pu(IV) hydroxocarbonato complexes (in analogy with Th) are suggested to be formed (Yamaguchi et al. 1994). In the NEA review of Pu(IV) (Lemiere 2001, Guillamont et al. 2003), formation constants for carbonate complexes $Pu(CO_3)_4^{4-}$ and $Pu(CO_3)_5^{6-}$ are only selected. In this report it is for the sake of conservatism taken that, analogically to Th(IV), Pu(IV) also forms anionic hydroxocarbonato complexes.

The proportion of Pu(IV) in the waters is given in Table Pu-10. The proportion of Pu(IV) increases with increase of pH and on the other hand with increase of pe (less reducing conditions).

Sorption of Pu(IV) is derived from the R_d values in nearly carbonate-free Cs-added OLKR5 water in initially aerobic (mildly reducing) conditions (Table 2 in Kulmala et al. (1998)). The R_d values for the crushed rocks had ranges 55.8 – 93.3, 51.9 – 84.4 and 27.4 – 186 m^3/kg for mica gneiss (OLMG), tonalite (OLTON) and granite (OLGR) respectively. The R_d values for the reference rocks in OLKR5 water were derived by multiplying the experimental R_d values by the ratio of the micaceous minerals and hornblende in the reference rocks to the experimental rocks. The R_d values were converted to the K_d values using the crushed rock to intact rock conversion factors for the reference rocks. The derived K_d values are given in Table Pu-10. Uncertainty in differences in mineral compositions, especially of the amounts of micaceous minerals and hornblende between the rocks used in Kulmala et al. (1998) and the reference rocks, is smallest for the mica gneisses (OLMG and T-MGN) and P-TGG and between the granite (OLGR) and PGR rock. For this reason, K_d values 12 m^3/kg and 6 m^3/kg for T-MGN and P-TGG in OLKR5 water were adopted for the calculation of K_d values in the

reference waters. For T-TGG, the K_d value based on R_d for OLMG mica gneiss was selected. For PGR, the K_d values derived from R_d values for the low-mica rocks tonalite (OLTON) and granite (OLGR) was selected for further evaluation of K_d values in the reference waters.

Influence of carbonate on sorption of Pu(IV)

Only a small decrease of sorption of Pu(IV) on kaolinite in ambient atmospheric conditions (pCO_2 -3.5 atm) was reported by Banik et al. (2007a). Owing to the constant CO_2 partial pressure, the carbonate concentration in these experiments was much higher than in the reference waters. Comparison of sorption of Pu(IV) and Th in CO_2-free and ambient atmospheric conditions indicated differences in sorption between these actinides, especially at pH 5–6, but this cannot be attributed to carbonate complexation of Pu or Th.

Table Pu-9. *Proportion of Pu(IV) of total Pu in reducing reference waters (REF) and at pH 10.*

Water	REF	pH10
OLGA	0	1.0
ALLMR*	0.95	1.0
KR4_81_1	0.005	0.3
OLBA/KR6_135_8	0.01	1.0
KR20_465_1	0.01	1.0
OLSR(low CO_3^-)	1.0	1.0

Table Pu-10. *K_d values (m^3/kg) of Pu(IV) for Olkiluoto reference rocks in OLKR5 water converted from the R_d data for Olkiluoto rocks in Kulmala et al. (1998).*

Data rock		T-MGN	P-TGG	T-TGG	PGR
OLMG	range	10 – 16	5 – 7	1.9 – 3.0	0.4 – 0.7
	mean	12	6	2.5	0.5
OLTON	range	19 – 29	8 – 14	3.6 – 5.5	0.8 – 1.2
	mean	26	12	5.0	1.1
OLGR	range	12 – 29	5 – 22	3.2 – 9	0.5 – 2.0
	mean	22	13	5.2	1.1

For Th, there was no reduction of sorption at the pH where the speciation modelling indicated high impact of Th-hydroxocarbonato complexes. As suggested by the results in Banik et al. (2007a, b), no difference due to carbonate is assumed for Pu(IV) and Th(IV) at pH 6–10. The K_d values of $Pu(OH)_4$ are given in Table Pu-11. The best estimate K_d values for Pu are derived from these values, using the proportion of $Pu(OH)_4$ as the conversion factor. These values are given in Table Pu-12.

Correction for K_d values for low pH in OLGA

In mildly oxidising conditions in the glacial melting water OLGO at pH 5.8, plutonium is tetravalent Pu(IV) and $Pu(OH)_4$ is the main species as shown for ALLMO water (Figure Pu-8). For Th, the K_d values at pH 6 were 1/3 times the value at pH 7-8. The same correction is made to K_d value Pu(IV) in OLGA, and K_d for $Pu(OH)_4$ is 4 m^3/kg (Table Pu-11). At pH 5.8 $Pu(OH)_4$ is not the sorption determining species in any of the waters in reducing or oxidising conditions.

Sorption at pH 10

At pH 10 under reducing and mildly reducing conditions, $Pu(OH)_4$ is the dominant sorbing species in all reducing waters. The proportion of $Pu(OH)_4$ at pH 10 is given in Table Pu-9, the K_d values for $Pu(IV)(OH)_4$ in Table Pu-11 and K_d of Pu in Table Pu-12.

Table Pu-11. *K_d values (m^3/kg) of $Pu(IV)(OH)_4$ for the rocks in the reference waters.*

Rock	T-MGN	P-TGG	T-TGG	PGR
All waters pH 8-10	12	6	2.5	1
OLGA pH 5.8	4	2	0.8	0.3

Table Pu-12. *Best estimate K_d values (m^3/kg) of Pu for Olkiluoto reference rocks in the reference waters. Values are given only to conditions where Pu(IV) is the main oxidation state or estimated to have largest impact on sorption. The carbonato complexes in KR4_81_1 water at pH 10 are taken as non-sorbing species.*

Rock		T-MGN	P-TGG	T-TGG	PGR
Water	pH				
OLSR	8.3	12	6	2.5	1
ALLMR*	8.8	12	6	2.5	1
OLGA	10	12	6	2.5	1
KR4_81_1	10	4	2	0.8	0.3
OLBA	10	12	6	2.5	1
KR20_465_1	10	12	6	2.5	1
OLSR	10	12	6	2.5	1
*mildly reducing (Figure Pu-6)					

NOTE

At the reference pH to the waters in OLGA, KR20- , KR4 and OLBA/KR6, sorption is determined by sorption of Pu(III). The K_d values for these waters are given in Tables Pu-10 and Pu-13.

24.2.5 Lower limit K_d values for Pu(IV) in conditions where Pu(IV) is the main oxidation state

The uncertainties in the estimation of K_d values for the rocks originates from the mineralogical uncertainties, and at high pH also the possible effect of decrease of sorption at higher pH, as suggested by Sabodina et al. (2006) and Banik et al. (2007a,b).

The K_d values were converted from data for Olkiluoto rocks in OLKR5 water. The uncertainty in pH of the experimental conditions is not regarded as causing large errors in the K_d estimations. The largest uncertainty is from the mineralogical heterogeneity of the rock compositions and conversion of R_d values to K_d values. Transfer of R_d values in OLKR5 water to the reference waters was made in a conservative way. It is thus regarded as sufficient to use a total uncertainty factor of 20 for T-MGN, P-TGG and T-TGG and 50 for PGR. The lower limit values are given in Table Pu-13.

24.3 Sorption in aerobic/oxidising conditions

24.3.1 Source data

In Kulmala et al. (1998), R_d values in aerobic Romuvaara and Kivetty fresh groundwaters were (0.045 – 0.61 m^3/kg) for the granitic rocks from the Romuvaara and Kivetty sites (Table 3 in Kulmala et al. (1998)). K_d values for oxidising conditions were converted from experimental R_d values under aerobic conditions in RoKR4 water in Kulmala et al. (1998). Conversion to R_d values for reference rocks was undertaken using the ratio of the proportions of micaceous minerals and hornblende of the rocks and converting R_d values to K_d values for intact rocks using the conversion factors for the reference rocks (Chapter 3). The K_d values are indicated in Table Pu-14. At pH 7–10, the mean K_d values derived for the rocks in the low-carbonate Ro water in Kulmala et al. (1998) are $1.0 \cdot 10^{-3}$ to $1.2 \cdot 10^{-1}$ m^3/kg.

Table Pu-13. *Lower limit K_d values (m^3/kg) of Pu(IV) for Olkiluoto reference rocks in Olkiluoto reference waters. Values are given only to conditions where Pu(IV) is the main oxidation state or estimated to have largest impact on sorption.*

ROCK		T-MGN	P-TGG	T-TGG	PGR
Water	pH				
ALLMR*	8.8	6.0E-01	3.0E-01	1.3E-01	5.0E-02
OLSR	8.3	6.0E-01	3.0E-01	1.3E-01	5.0E-02
OLGA	10	6.0E-01	3.0E-01	1.3E-01	5.0E-02
ALLMR	10	6.0E-01	3.0E-01	1.3E-01	5.0E-02
OLBA	10	6.0E-01	3.0E-01	1.3E-01	5.0E-02
KR20_465_1_1	10	6.0E-01	3.0E-01	1.3E-01	5.0E-02
OLSR	10	6.0E-01	3.0E-01	1.3E-01	5.0E-02
*mildly reducing (Figure Pu-6)					

Table Pu-14. *Mean K_d values (m^3/kg) for the Olkiluoto reference rocks derived from R_d values (Kulmala et al. 1998) for RoTon (tonalite), RoGR (granite) and RoMG (mica gneiss) under aerobic conditions in fresh Romuvaara groundwater (pH 7.9).*

Rock	T-MGN	P-TGG	T-TGG	PGR
RoTon	0.055	0.013	0.011	0.0020
RoGR	0.142	0.039	0.027	0.0055
RoMG	0.030	0.014	0.0058	0.0012

Effect of carbonate concentration on sorption of Pu under oxidising conditions

In their study of sorption of Pu on granitic biotite, Furya et al. (1997) determined sorption in 0.1 M NaCl at pCO_2 1 $\cdot 10^{-3.5}$. The highest sorption (R_d 0.7 m^3/kg) was at pH 6–8, and R_d value decreased to 0.09 m^3/kg at pH 10. The decrease was modelled to be due to the increase of anionic Pu(V) and Pu(VI) carbonato complexes with pH. No other data on the sorption of Pu(V/VI) in high-pH solutions on rock or mineral material have come to the attention of the authors of this report.

24.3.2 Best estimate K_d values in aerobic conditions

Under oxidising conditions, the results of speciation calculation indicate the presence of Pu(IV), Pu(V) and Pu(VI). In aerobic shallow waters, Pu(V) was determined as the main oxidation state in Choppin & Morgenstern (2001). Experimental findings on Pu(V) and Pu(VI) in natural waters and groundwater simulants have confirmed that the presence of these higher oxidation states is possible, but Pu at the higher oxidation states is easily reduced to Pu(IV). In solutions that contain humic substances or bacteria (B. subtilis), Pu(VI) was not stable but was reduced to Pu(IV) and Pu(III/IV) (Ohnuki et al. 2007, 2009, Banik et al. 2007b). Pu(VI) has been shown to be relatively stable in 0.01 M NaCl at pH 5 when contacted to kaolinite clay (BET/N_2 26.4 m^2/g) and in the absence of organic substances (Ohnuki et al. 2007).

The K_d values for the rocks are estimated in the glacial melt water OLGO, fresh ALLMO and saline OLSO reference waters. The best estimate value for T-MGN is the mean value for K_d values derived from the data for the rocks in Kulmala et al. (1998) shown in Table Pu-14 above. It is taken that the impact of Pu(IV) is negligible.

No data on sorption of Pu(V,VI) in glacial melt water and saline waters were available and results for Np(V) are applied to the calculation of K_d value in OLGO and OLSO waters. For OLGO water, the K_d of Pu at pH 5.8 is derived from the K_d in fresh water at about pH 8. The K_d in OLGO is proposed to be 1/40 times the value at about pH 8 in the source data (see sorption of Np(V) on kaolinite in Chapter 22). Sorption of Np(V) at pH of the other waters was the same at different ionic strengths. For Pu, the same best estimate K_d values are proposed in the ALLMO and OLSO waters (Table Pu-15).

Table Pu-15. *Best estimate K_d values of Pu (m^3/kg) in oxidising conditions in OLGO, ALLMO and OLSO waters at the pH of reference water.*

Rock		T-MGN	P-TGG	T-TGG	PGR
Water	pH				
OLGO	5.8	2.0E-03	1.0E-03	5.0E-04	1.0E-04
ALLMO	8.4	7.0E-02	2.0E-02	2.0E-02	3.0E-03
OLSO	7.2	7.0E-02	2.0E-02	2.0E-02	3.0E-03

Table Pu-16. *Best estimate K_d values (m^3/kg) of Pu in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at pH of 10.*

Rock		T-MGN	P-TGG	T-TGG	PGR
Water	pH				
OLGO	5.8	2.0E-03	1.0E-03	1.0E-03	4.0E-04
ALLMO	8.4	6.0E-04	3.0E-04	3.0E-04	1.0E-04
OLSO	7.2	2.0E-03	1.0E-03	1.0E-03	4.0E-04

Sorption at pH 10

No sorption results of Pu(V,VI) on rocks at pH 10 have come to the attention of the authors. Decreases of R_d values with increasing pH for biotite in Furya et al. (1997) were difficult to interpret. Sorption of Pu (V/VI) at pH 10 on the rocks is proposed to be the same as that of Np(V), as an analogue to Pu (V/VI). The best estimate K_d values are in Table Pu-17.

24.3.3 Lower limit K_d values in aerobic values

The R_d values used for derivation of the best estimate K_d values from data in Kulmala et al. (1998) may have been influenced by trace concentration of Pu(IV) in the waters, as suggested by the speciation calculations. Due to this uncertainty the lower limit K_d values derived to Np(V) are proposed for Pu(V,VI) in all waters at reference pH and at pH 10. The lower limit K_d values for the rocks are shown in Tables Pu-17 – Pu-20.

Table Pu-17. *Lower limit K_d values (m^3/kg) of Pu for T-MGN Olkiluoto mica gneiss in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

T-MGN			
pH	OLGO	ALLMO	OLSO
REF	**1.0E-06**	**3.0E-05**	**3.0E-06**
10	1.0E-04	3.0E-05	1.0E-04

Table Pu-18. *Lower limit K_d values (m^3/kg) of Pu for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

P-TGG			
pH	OLGO	ALLMO	OLSO
REF	**5.0E-07**	**2.0E-05**	**2.0E-06**
10	5.0E-05	2.0E-05	5.0E-05

Table Pu-19. *Lower limit K_d values (m^3/kg) of Pu for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

T-TGG			
pH	OLGO	ALLMO	OLSO
REF	**4.0E-07**	**2.0E-05**	**4.0E-05**
10	4.0E-05	2.0E-05	2.0E-06

Table Pu-20. *Lower limit K_d values (m^3/kg) of Pu for PGR Olkiluoto pegmatitic granite in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

PGR			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-08**	**2.0E-06**	**2.0E-07**
10	2.0E-06	2.0E-06	2.0E-06

24.4 Sorption on clays

24.4.1 Sorption of Pu(III)

No relevant data on sorption of Pu(III) on the clays have come to the attention of the authors of this report. The same K_d values as for Eu(III) are suggested as the best estimate and lower limit values for Pu(III) in reducing conditions. The best estimate K_d values are shown in Tables Pu-21 – Pu-24. In ALLMR and OLSR at reference pH, sorption is determined by Pu(IV).

Table Pu-21. *The best estimate K_d (m^3/kg) values of Pu(III) for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**5.0E+00**	**4.8E+02**	**3.0E+02**	**6.0E+02**	**3.0E+02**	**3.0E+01**
10	6.0E+02	5.4E+02	5.4E+02	5.4E+02	9.0E+00	5.4E+02

Table Pu-22. *The best estimate K_d (m^3/kg) values of Pu(III) for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**1.0E+02**	**2.0E+02**	**2.5E+02**	**2.5E+02**	**2.5E+02**	**2.5E+02**
10	2.5E+02	2.3E+02	2.3E+02	2.3E+02	4.0E+00	2.3E+02

Table Pu-23. *The lower limit K_d (m^3/kg) values of Pu(III) for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.4E-01**	**5.3E+01**	**1.4E+01**	**6.6E+01**	**1.4E+01**	**1.0E+00**
10	2.9E+01	5.9E+01	2.6E+01	5.9E+01	4.3E-01	2.6E+01

Table Pu-24. *The lower limit K_d (m^3/kg) values of Pu(III) for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. KR4 = KR4_81_1 ; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4 *	KR20 *
REF	**1.1E+01**	**3.7E+01**	**2.1E+01**	**4.6E+01**	**2.1E+01**	**1.3E+01**
10	2.1E+01	4.2E+01	1.9E+01	4.2E+01	3.3E-01	1.9E+01
*experimental sorption values show no reduction due to carbonate complexation						

24.4.2 Sorption of Pu(IV)

No relevant data on sorption of Pu(IV) on the clays have come to the attention of the authors of this report. Limited data on sorption on kaolinite indicated similar sorption of Pu(IV) and Th(IV) at the pH region of interest in this report. The same best estimate and lower limit K_d values as for Th are proposed in the reference pH conditions (ALLMR, OLSR), where Pu(IV) is the dominant species. At pH 10 in all waters, sorption is determined by sorption of Pu(IV). At pH 10 in KR4 water, the proportion of Pu(IV)(OH)4 is 30 % and the Kd values at pH 10 are corrected to 0.3 times that in the other waters. The best estimate values for kaolinite and illite are given in Tables Pu-25 – Pu-26 and the lower limit values in Tables Pu-27 – Pu-28.

Table Pu-25. *Best estimate K_d values (m^3/kg) of Pu for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**6.0E+01**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**	**2.0E+02**
10	2.0E+02	2.0E+02	2.0E+02	2.0E+02	6.0E+01	2.0E+02

Table Pu-26. *Best estimate K_d values (m^3/kg) of Pu for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**	**2.0E+01**
10	2.0E+01	2.0E+01	2.0E+01	2.0E+01	6.0E+00	2.0E+01

Table Pu-27. *Lower limit K_d (m^3/kg) values of Pu for kaolinite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Kaolinite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**2.7E+01**	**8.4E+01**	**8.3E+01**	**8.4E+01**	**6.0E+01**	**6.0E+01**
10	8.4E+01	8.4E+01	8.4E+01	8.4E+01	2.5E+01	6.0E+01

Table Pu-28. *Lower limit K_d (m^3/kg) values of Pu for illite at Olkiluoto at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold. Waters KR4 = KR4_81_1; KR20 = KR20_465_1.*

Illite						
pH	OLGA	ALLMR	OLBA	OLSR	KR4	KR20
REF	**7.5E+00**	**7.5E+00**	**7.5E+00**	**7.5E+00**	**5.3E+00**	**5.3E+00**
10	7.5E+00	7.5E+00	7.5E+00	7.5E+00	2.3E+00	5.3E+00

24.4.3 Sorption of Pu(V,VI)

No relevant data on sorption of Pu(V) nor Pu(VI) on the clays has come to the attention of the authors of this report. For this reason, Np(V) is used as the chemical analogue to Pu(V,VI). The same best estimate and lower limit K_d values as for Np(V) under aerobic conditions are proposed for Pu(V,VI). The best estimate values are given in Tables Pu-29 and Pu-30 and the lower limit values in Tables Pu-31 and Pu-32.

Table Pu-29. *Best estimate K_d values (m^3/kg) of Pu for kaolinite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

Kaolinite			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-03**	**2.0E-01**	**2.0E-02**
10	3.0E+00	1.0E-01	3.0E+00

Table Pu-30. *Best estimate K_d values (m^3/kg) of Pu for illite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

Illite			
pH	OLGO	ALLMO	OLSO
REF	**1.4E-02**	**5.0E-02**	**1.6E-02**
10	1.0E+00	4.0E-02	1.0E+00

Table Pu-31. *Lower limit K_d values (m^3/kg) of Pu for kaolinite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

Kaolinite			
pH	OLGO	ALLMO	OLSO
REF	**2.0E-04**	**2.0E-02**	**2.0E-03**
10	3.0E-01	1.0E-02	3.0E-01

Table Pu-32. *Lower limit K_d values (m^3/kg) of Pu for illite in Olkiluoto in aerobic/oxidising groundwaters OLGO, ALLMO, OLSO at the pH of reference water (REF) and at pH 10. K_d values at the pH of reference water are marked with bold.*

Illite			
pH	OLGO	ALLMO	OLSO
REF	**1.0E-03**	**4.0E-03**	**1.0E-03**
10	1.0E-01	3.0E-03	1.0E-01

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APPENDIX 1 Composition of rock samples

***Table A1-1**. Average mineral compositions (vol %) of the studied rocks from Olkiluoto area and their standard deviation (Kärki & Paulamäki 2006).*

Mineral	T-MGN gneiss	T-TGG gneiss	P-TGG gneiss	Peg granite
Quartz	31±10	33±3	24±6	35±14
Plagioclase	17±7	23±6	34±8	17±9
K-feldspar	6.4±3.7	20±9	12±11	33±18
Biotite	21±8	8.2±7.5	23±7	0.9±1.7
Muscovite	0.7±0.7	1±1.2	0.3±0.5	2.5±2.8
Hornblende	0.3±0.4	0±0.1	0.6±2.2	0±0
Pyrite	0.1±0.2	0±0.1	0.1±0.2	0±0
Chlorite	3.8±5.2	1.7±1.9	0.3±0.5	0.7±0.9
Cordierite	0.9±1.6	0±0.1	0.1±0.2	0.1±0.4
Pinite	9.2±7.6	1.3±2.6	0.1±0.2	0.4±1.7
Garnet	0.1±0.2	1.2±3.6	0.4±0.8	0.4±1
Sillimanite	1.3±2.9	0±0.1	0.1±0.2	0.4±1.3
Epidote	0.2±0.2	0.1±0.2	0.1±0.2	0±0.2
Sphene	0.2±0.2	0.1±0.1	0.1±0.2	0±0
Apatite	0.2±0.2	0±0.1	1±1	0±0.1
Saussurite	5.8±6.1	8.9±5.6	4.5±3.7	7.5±5.9
Sericite	0.3±0.4	0.6±1.8	0.3±0.6	1.2±2.9
Opaques	1.6±2.4	0.5±0.6	0.5±0.6	0.4±0.5

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***Table A-2.** Particle size distribution of crushed rock samples.*

Sample	< 2.0 mm (%)	<0.5 mm (%)	<0.25 mm (%)	<0.125 mm (%)	<0.063 mm (%)
T-MGN	100	49.3	31.5	18.1	10.1
P-TGG	100	50.4	32.4	16.6	7.9
T-TGG	100	39.8	24.6	16.4	7.0
PGR	100	42.7	25.7	14.4	8.1

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GEOLOGICAL SURVEY OF FINLAND

Geological Survey of Finland
Research Laboratory, Espoo

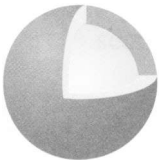
Research report CM **16/2005/3**

Mineral description and concentration of mica from granodiorite/mica-gniess, Olkiluoto, Finland

Tegist Chemet, Antero Lindburg, Jukka Marmo

June, 2005

Tilaaja: Posiva Oy 9699/05/ARIK
GTK Project no.: 1803022, 2802001



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Sample:

Two types of drill core samples (granodiorite and mica gneiss), about 10-12kg, were submitted to research laboratory, GTK, Espoo to study the samples and concentrate mica.

Microscopic observation:

Sample A (granodiorite):

According to a few thin sections observation, the rock generally contains feldspar, quartz and mica as major minerals. Biotite is the main type of mica that constitutes 10-15vol % of the rock. Minor amount of muscovite and chlorite are observed as a result of alteration of biotite. Biotite is generally fine grained. But grains size range from about O.Smm to 1.5mm is not uncommon. Biotite deposited along grain boundaries of quartz and feldspars, and filling interstices between minerals. It has a tendency of being oriented but commonly randomly deposited . Feldspar is generally in the form of k-feldspar and plagioclase, subhedral to anhedral in shape. Feldspars are often chocked by sericite alteration. Grain size reaches up to 4-Smm in length. The other major rock-forming mineral is quartz, which is as well subhedral to anhedral in shape with common andulus extinction. The grain size ranges from O.lmm to 2mm. Small rounded grains of quartz are commonly observed as inclusion in feldspar grains. Epidote, apatite and opaque are found as accessory minerals. See Table 1 for mineral content according to point counting.

Sample B (Mica gneiss):

Similarly as sample A, the rock is composed of three major minerals: mica, feldspars and quartz. Mica mainly as biotite is generally oriented with grain size ranges from about lOOj.lm to about l.Smm. It constitutes 15-30vol% of the rock, varying from one thin section to another. Alteration to chlorite and muscovite is quite rare but in comparison

alteration is more of to muscovite rather than to chlorite. Feldspar is common in the form of k-feldspar (e.g., microciine) and plagioclase. Grain size is relatively finer than sample A. It ranges from about 0.2mm to l.Smm, and rather equigranular but often anherdral. Feldspar is commonly chocked by sericite as a result of alteration. Quartz is as well anherdal and equigranular. It is more common than feldspars in some section. The grain size ranges from about O.lmm to 1mm. Fine-grained quartz (<O.lmm) is often found as inclusions in feldspar. Accessory minerals are garnet, cordierite, sillimanite, apatite and opaque. See also Table 1 for point counting result.

Table 1. Mineral composition of granodiorite (A) and mica gneiss (B) samples from Olkiluoto; Volume-% of minerals calculated according to point counting, 500points/section

	A9	A2	A1	B8	B2	B9
Quartz	24.4	25.8	24.2	33.6	31.6	27.6
Plagioclase	38.8	40.8	42.6	14.6	26.8	23.0
K-feldspar	17.4	11.4	14.6	10.2	10.2	7.8
Biotite	**11.4**	**18.4**	**16.2**	**32.4**	**20.2**	33.8
Muscovite/ sericite	3.4	2.2	1.0	5.4	2.0	2.4
Chlorite	3.8		0.2			
Epidote	0.8	+	0.8			+
Apatite	+	0.6	0.4	0.2		0.6
Sillimanite				2.6	1.0	4.0
Cordierite					7.4	
Opaques	+	0.8	+	1.0	0.8	0.8
	100.0	100.0	100.0	100.0	100.0	100.0

Note on separation procedures:

Sample weight: 10-12kg

Crushing: The two samples are separately crushed usmg Roller crusher, before grinding, to reduce the particle size to <3 mm in diameter and to minimize the production of fine particles.

Grinding:

Sample: sample A= 4kg, sample B= 6kg

Mill: a laboratory rod mill (180mm by 250mm in diameter)

Rod charge: about 30% of the mill volume

Capacity: 1kg sample (with a kg capacity, 10 batches of grinding were performed)

Pulp density: 50% solid

Grinding time: 10-12min. (important variable controlling the liberation and size distribution)

Particle size distribution:

According to microscope observation, the mineral particles are well liberated. Although the particle size measurements were made after desliming the ground sample, it shows the general size distribution of particles after rod mill grinding (Table 1, Fig 1). About 90% of the sample is less than 250 microns and 40% is less than 90 microns; major parts of the fine particles are deslimed. The given figure is an adequate distribution for consecutive processes to separate mica from quartz and feldspars (either be flotation, magnetic separation or heavy liquid separation).

Table 1. Particle size distribution of sample A, after rod mill grinding and desliming

Sieve size	Wt (g)	Wt(%)	Cum wt(%)
>250	10.87	10.85	100.00
180-250	24.72	24.67	89.15
120-180	22.3	22.26	66.89
90-120	16.57	16.54	50.35
63-90	10.67	10.65	39.70
45-63	7.79	7.78	31.93
32-45	3.05	3.04	28.89
20-32	3	2.99	25.89
<20	1.22	1.22	24.67
	100.19		

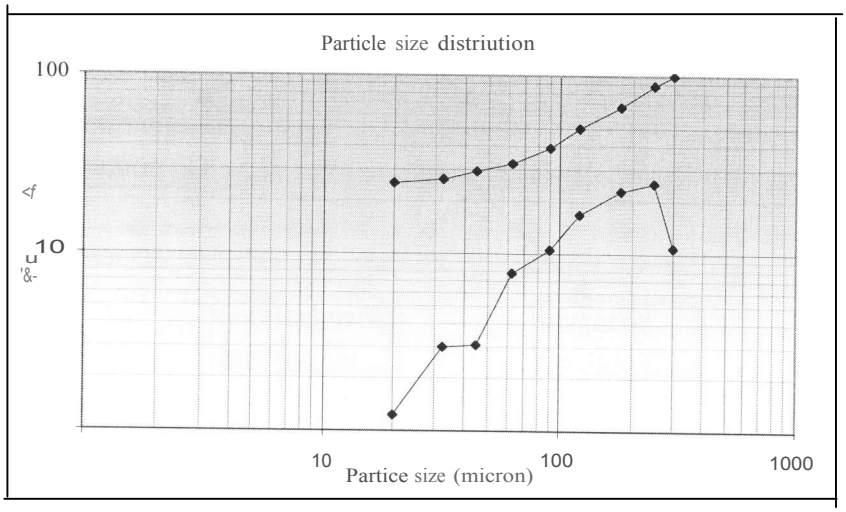

Fig 1. Graphic representation of Table 1. as wt % particle size distribution and cumulative wt% passing

High Intensity Magnetic Separation (HIMS):

HIMS is used to preconcentrate mica and reduce the amount of feldspars and quartz. Three fractions were produced from each sample (A and B). The first run, 1.5kg sample, was run with 30% field strength (gradient 0.5Tesla). Magnetic fraction of the first run was repeated with about 11% (0.1Tesla) field strength. As a result two nonmagnetic fractions and one magnetic fraction were produced (See fig 2.)

Separator:	Sala wet HMS
Capacity:	1.5- 2kg
Pulp density:	10% solid
Matrix size:	850!-lm tube
Field strength:	0.5Tesla (30%) and 0.1Tesla (11%)
Dispersant:	no

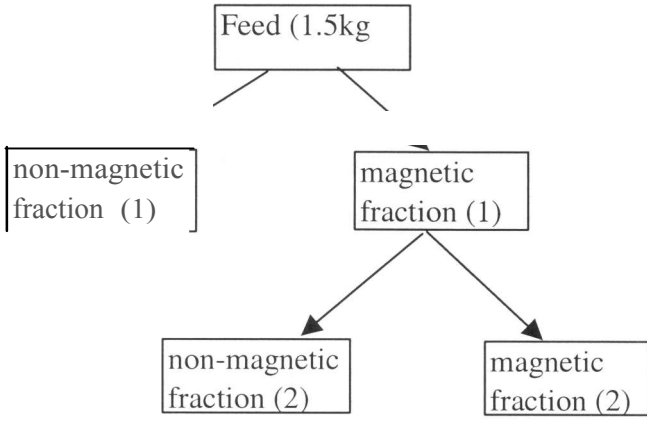

Fig 2. Schematic presentation of the HIMS steps

Heavy liquid media separation:

The magnetic fraction (2) that contains 65-70% of mica was taken to heavy liquid separation. This process is based on the specific gravity difference between mica and the rest of major minerals (mainly quartz and feldspar). Mica (biotite) is 2.7- 3.3, feldspars are 2.6 – 2.76 and quartz is 2.26 – 2.65. The heavy liquid used is Bromoform with the density of 2.82. Mica is concentrated as heavies and separation is repeated to concentrate as good grade mica as possible. The capacity of the single separation process was up to 0.5kg sample.

The final mica concentrate is washed using isopropyl from any bromoform on the mica surface and dried.

Summary on results:

The grinding parameters were set based on expenences of grinding different type of rocks and ores. As a result, sufficient liberation of mica with proper particle size distribution, adequate for consecutive processes, was achieved. Some lose of sample was unavoidable due to desliming and dewatering processes. The ground samples were treated by wet high intensity magnetic separation (HIMS) and the process produced three

fractions from each samples (Table 2). Only the last magnetic fraction, which contains up to 65-70% mica, was taken for heavy liquid separation to upgrade the mica concentrate. Mica concentration was upgraded to 85-90% with two stages of concentration using heavy liquid (Table 3). Depending on the amount of original sample and its mica content, about 290g and 500g of mica concentrate were produced from Sample A and B, respectively. If further concentration of mica is needed, the non-magnetic fraction (2) can be used that still contains up to 40-50% mica.

Table 2. Weight fractions from high intensity magnetic separation

Sample	Non-magnetic fraction (1)	Non-magnetic fraction (2)	Magnetic fraction (2)
Sample A– 3.7kg	2046g	1071g	472g
Sample B– 5.2kg	2260g	1995g	730g

Table 3. Weight fractions from heavy liquid separation

Sample	Magnetic fraction (2)	Density <2.8	Density > 2.8
Sample A	472g	181g	290g
Sample B	730g	220g	507g

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APPENDIX 2 Composition of clays

Table A-3. *Composition of kaolinite, illite and chlorite (*http://www.clays.org).

	Kaolinite KGa-1b (low-defect)	**Illite IMt-1**	**Ripidolite CCa-2 (Chlorite)**
Origin	Tuscaloosa, County of Washington, State of Georgia, USA	Silver Hill, Montana, USA	Flagstaff Hill, El Dorado County, California, USA
Chemical composition (%)			
SiO_2	44.2	49.3	26.0
$Al2O_3$	39.7	24.25	20.0
TiO_2	1.39	0.55	0.476
Fe_2O_3	0.13	7.32	26.6
FeO	0.08	0.55	20.8
MnO	0.002	0.03	0.1
MgO	0.03	2.56	17.2
CaO	n.d.	0.43	0.25
Na_2O	0.013	0	<0.1
K_2O	0.05	7.83	><0.1
F	0.013	-	-
P_2O_5	0.034	0.08	0.02
CEC(meq/100g)	2.0	17.0*	-
SA(N_2) (m^2/g)	10.05 +/- 0.02 11.1 -11.6***	11* 6.4***	1.1 +/- 0.1** 2.6***

*O'Loughlin, E.J., Traina, S.J., Sims, G.K. 2000. Effects of sorption on the biodegradation of 2-methylpyridine in aqueous suspensions of reference clay minerals. Environ.Toxicol. Chem. 19, 2168–2174.

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***In-house data.

APPENDIX 3 Composition of reference waters

Table A-4*. Composition of reference waters (Vuorinen & Snellman 1998)*

	Fresh groundwater			Saline groundwater			Glacial meltwater		Brackish groundwater	
(mM)	ALL	ALLMO	ALLMR	OLSO	OLSR	KR20	OLGO	OLGA	OLBA	KR4
HCO_3^-	2	1.5	1.1	0.16	-	0.657	0.0032	-	1.6	4.57
SiO_2	0.2	0.05	0.03	0.04	-	0.166	0.002	0.002	0.07	0.200
Na^+	2.3	2.3	2.3	209.1	208.8	144.8	0.03	0.03	76.0	13.1
K^+	0.10	0.10	0.10	0.54	0.54	0.28	0.015	0.015	17.8	0.25
Ca^{2+}	0.45	0.25	0.13	99.8	100	32.4	0.01	0.01	0.70	1.4
Mg^{2+}	0.11	0.11	0.03	2.3	2.3	2.55	0.01	0.01	6.2	0.741
Sr^{+2}	-	-	-	0.40	0.40	0.16	-	-	0.01	0.006
B^{3+}	-	-	-	0.08	0.08	0.120	-	-	0.06	0.027
SO_4^{2-}	0.10	0.10	0.10	0.044	0.044	0.208	0.0021	0.0021	4.7	0.958
Cl^-	1.2	1.3	1.4	412.9	412.7	180.5	0.086	0.086	78.9	9.90
F^-	-	-	-	0.063	0.063	0.0526	-	-	0.016	0.032
Br^-	-	-	-	1.31	1.31	0.5506	-	-	0.163	0.0175
I^-	-	-	-	0.007	0.007	-	-	-	-	-
NH_4^+	-	-	-	-	-	<0.001	-	-	0.018	0.0419
pH_{cal}	8.3	8.4	8.8	7.2	8.3	7.4	5.8	5.8	7.6	7.8

Table A-5 *Recipes of reference waters presented in Hellä et al. 2014.*

OLGA pH 5.8				**OLGO pH 5.8**			
Composition	mg/L	**Chemicals**	mg/L	**Composition**	mg/L	**Chemicals**	mg/L
Na	0.60	NaCl	1.3307	Na	0.60	NaCl	1.3307
K	0.6	KCl	0.8337	K	0.60	KCl	0.8337
Ca	0.52	$CaCl_2 \cdot 2H_2O$	1.9075	Ca	0.52	$CaCl_2 \cdot 2H_2O$	1.9075
Mg	0.30	$MgCl_2 \cdot 6H_2O$	2.5094	Mg	0.30	$MgCl_2 \cdot 6H_2O$	2.5094
SiO_2	0.10	$Na_2SiO_3 \cdot 9H_2O$	0.4730	SiO_2	0.10	$Na_2SiO_3 \cdot 9H_2O$	0.4730
Cl	3.06			Cl	3.06		
SO_4	0.20	K_2SO_4	0.7256	SO_4	0.20	K_2SO_4	0.7256
HCO_3	-			HCO_3	0.196		
OLBA pH 7.6							
Composition	mg/L	**Chemicals**	mg/L				
Na	1750	NaCl	3777				
K	18.9	KCl	22.62				
Ca	84.5	$CaCl_2 \cdot 2H_2O$	310.0				
Mg	26.5	$MgCl_2 \cdot 6H_2O$	221.3				
Cl	2530						
SO_4	458	Na_2SO_4	676.8				
Br	13.1	KBr	19.56				
F	0.30	KF	0.91				
Sr	0.10	$SrCl_2 \cdot 6H_2O$	0.30				
NH_4	0.33	NH_4Cl	0.98				
SiO_2	6.1	$Na_2SiO_3 \cdot 9H_2O$	28.92				
B	0.62	H_3BO_3	3.55				
HCO_3	111	$NaHCO_3$	152.8				

ALLMR pH 8.8				**ALLMO 8.4**			
Composition		**Chemicals**		**Composition**		**Chemicals**	
	mg/L		mg/L		mg/L		mg/L
Na	52.5	NaCl	56.24	Na	52.5	NaCl	40.95
K	3.9	KCl	7.46	K	3.9	KCl	7.46
Ca	5.1	$CaCl_2 \cdot 2H_2O$	18.85	Ca	10.2	$CaCl_2 \cdot 2H_2O$	37.54
Mg	0.7	$MgCl_2 \cdot 6H_2O$	5.97	Mg	2.8	$MgCl_2 \cdot 6H_2O$	2.88
SiO_2	1.7	$Na_2SiO_3 \cdot 9H_2O$	7.96	SiO_2	2.9	$Na_2SiO_3 \cdot 9H_2O$	13.76
Cl	48.8			Cl	47.5		
SO_4	9.6	Na_2SO_4	14.20	SO_4	9.6	$Mg_2SO_4 \cdot 7H_2O$	24.65
HCO_3	65.0	$NaHCO_3$	89.56	HCO_3	0.7	$NaHCO_3$	124.91
OLSR pH 8.3				**OLSO pH7.2**			
Composition		**Chemicals**		**Composition**		**Chemicals**	
	mg/L		mg/L		mg/L		mg/L
Na	4800	NaCl	12115	Na	4800	NaCl	12119.3
K	21	KCl	39.55	K	21.0	KCl	39.54
Ca	4000	$CaCl_2 \cdot 2H_2O$	14672.2	Ca	4000	$CaCl_2 \cdot 2H_2O$	14672.2
Mg	54.6	$MgCl_2 \cdot 6H_2O$	456.5	Mg	5.9	$MgCl_2 \cdot 6H_2O$	467.6
Sr	35.0	$SrCl_2 \cdot 6H_2O$	106.5	Sr	35.0	$SrCl_2 \cdot 6H_2O$	106.7
SiO_2	-			SiO_2	2.5	$Na_2SiO_3 \cdot 9H_2O$	11.83
Cl	14500			Cl	4500		
SO_4	4.2	Na_2SO_4	6.21	SO_4	4.2	Na_2SO_4	6.21
Br	104.7	NaBr	134.8	Br	104.7	NaBr	134.8
F	1.2	NaF	2.63	F	1.2	NaF	2.63
B	0.92	H_3BO_3	5.26	B	0.92	H_3BO_3	5.26
I	0.9	KI	1.11	I	0.9	KI	1.11
HCO_3	-			HCO_3	10.0	$NaHCO_3$	13.83

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APPENDIX 4 Methodology of batch experiments

METHODOLOGY OF BATCH EXPERIMENTS

New in-house elements for the evaluation of radioactive waste nuclides in Posiva's spent nuclear fuel safety assessment were Mo, Nb, Pa, Se, Sn, Th and U. The procedure of these experiments is briefly described and the experimental setup is summarised in Table A-6. The used materials are described in more detail in Chapter 2 and in the corresponding Appendices 1 and 2.

1 Modelling

The solution species and dissolution of the tracer element in the experimental conditions were calculated by PHREEQC (Parkhurst & Appelo 2003), using ANDRA's Thermo_Chimie Version 7b database (ANDRA 2009) to estimate the experimental conditions. For different water types, the speciation distribution was calculated in slightly reducing conditions and in oxidising conditions for each element, using appropriate solubility limiting phases. The added tracer (and carrier) concentrations were based on these calculations so as not to exceed the solubility of the element and avoid tracer (and carrier) precipitation before the experiment.

2 Solutions

2.1 Synthetic groundwaters

In batch sorption experiments, synthetic reference groundwater solutions (OLGA, ALLMR, OLBA, OLSR, OLGO, ALLMO, OLSO) were used. The nominal compositions of the solutions are described in Appendix 3.

All solutions were prepared to deionised water (Milli-Q) and pro analysis grade reagents. The oxygen-free solutions were prepared under a nitrogen or argon atmosphere. The water was degassed by boiling followed with nitrogen gas flow before transferring it to a glove-box. The experiments were run inside the anaerobic glove-box (MBraun 150MB-GH-B) or in-house made glove-box (argon), to prevent the interference of atmospheric carbon dioxide as well, especially in the alkaline solutions. The oxygen gas content was monitored during the experiment (Mbraun). In addition to the reference pH of the water, the pH of solutions was adjusted between 5.8 and 10. A solution with pH 10 corresponds to the effect of the cement plume. pH was adjusted with diluted HCl and NaOH (Merck, Titrisol). OLBA water could not be prepared below pH 8. In addition, the carbonate and calcium concentration had to be reduced to one tenth when preparing the pH 10 solution due to possible carbonate precipitation. In studies with carbonate, experiments below pH 7 were not performed due to the escape of carbon dioxide from the solution.

2.2 Buffer solutions

The buffers MES, MOPS, TRIS and CHES were used to regulate the pH during some sorption experiments (Perrin & Dempsey 1974). Their concentration was 10^{-3} M in sample solution.

2.3 Perchlorate solutions

0.1 M sodium and calcium perchlorate solutions were prepared of solid $NaClO_4 \cdot H_2O$ and $Ca(ClO_4)_2 \cdot 4H_20$ (Sigma-Aldrich, p.a.) in deionised water (Milli-Q). The studied pH range was adjusted using buffer solutions 4 to 10.

3 Solids

In batch sorption experiments, the selected rocks were tonalite granodiorite granite gneisses T-TGG and P-TGG, mica gneiss T-MGN and pegmatitic granite PGR with a maximum grain size of 2 mm. To keep the mineral composition unaltered, fine grained material was not removed. The average compositions of the rocks are presented in Appendix 1.

The used minerals were illite IMT-1 obtained from the American Clay Minerals Society Source Clays Repository and kaolinite KGa-1b from the reference clays of the American Clay Minerals Society. In Appendix 2 can be found the descriptions of these minerals. Illite was ground and sieved to a grain size below 0.149 µm. Kaolinite was already in fine grained form when obtained. The minerals were pre-treated to remove possible interferences during the sorption experiments, according to the method by Tournassat et al. (2007).

4 pH measurement

The pH was measured by Thermo Orion 3 Star or 920A meters using an Aquapro combination glass electrode. In calibration, commercial standard pH buffer solutions 4, 7 and 10 were used. The pH was also measured after the experiment ended. When buffers were not used in the experiments for the rocks and mineral samples, the pH may be changed from the initial value. pe was not followed in these experiments.

5 Radioactive tracers

Radioactive tracer were purchased from known commercial companies: Ni-63 (T½ = 100a), Se-75 (T½ = 119.78d, Eckert & Ziegler), Nb-93m (T½ = 16.13a, Isotrak AEA Technology QSA), Nb-95 (T½ = 34.97d, PerkinElmer, separated from Zr-95 solution), Mo-99 (T½ = 66h, MAP Medical Technologies Oy), Sn-113 (T½ = 115d, Eckert & Ziegler), Eu-152 (T½ = 13.5a), Pa-233 (T½ = 24d, which was separated from Np-237 by solvent extraction), U-233 (T½ = $1.6 \cdot 10^5$a, The Radiochemical Centre Amersham, England), ^{234}Th ($T_{1/2}$ = 24.2d, Merck, separated from solid p.a. $UO_2(NO_3)_2 \cdot 6H_2O$). The bulk solution was diluted to a suitable working concentration. If needed, a carrier was added or was already in the original bulk solution. The radioactivity was assayed by a

suitable method (see Table A-6 detection line). Background samples were prepared as actual samples.

6 Batch sorption method

The sorption experiments were performed by batch sorption and the mass distribution coefficient R_d (m^3/kg) was calculated according to ASTM batch tests methodology (ASTM 2001).

Samples were weighed in polyethylene vessels using a digital weighing balance with accuracy ± 0.0005. Mineral samples and crushed rock were immersed in solution for one day before adding the tracer to condition the solid material with the solution. The used solid to solution ratios are found in Table A-6. In the experiments, polyethylene vessels were used. When the sample size allowed, the solution was changed once before adding the tracer. At least two parallel samples were made. The experiments were mainly carried out in an N_2-atmosphere, few under ambient atmospheric conditions.

After tracer (and carrier) addition, the pH was adjusted using diluted carbonate-free HCl or NaOH solutions when necessary. The samples were stored in an end-over-end rotator during the experiment. After completing the experiment, the pH was measured. The contact time varied from three (minerals) to seven (rocks) days. All experiments were made at room temperature. Pipetting of solutions was performed with calibrated pipettes using good laboratory practice.

7 Separation of phases

The solid material was separated by centrifugation (3000 g, 10 min) and filtration (0.22µm µm Millex-GV Durapore). An aliquot for the radioactivity measurement was taken.

8 Mass distribution coefficient R_d

The mass distribution coefficient R_d (m^3/kg) was determined as follows:

$$R_d = \frac{C_i - C_f}{C_f} \frac{V}{m} \qquad (1)$$

where C_i and C_f are the activity concentrations in the initial solution and in the batch supernatants (Bq/m^3) at the end of the experiment, V is the volume of the liquid phase (m^3) and m is the mass of the crushed rock (kg dry weight).

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Table A-6. *Experimental setup. See detailed material descriptions in Chapter 2.*

	Nb	Se	U	Th
pH	5.8-10 (initial & final)	5.8-10 (initial & final)	7-10 (initial & final)	5.8-10 (initial & final)
S:L(g/mL)	rocks (1:20) minerals (0.02:20)	rocks (1:20) minerals (0.4:20&0.5:20)	rocks (1:20) minerals (0.05:20)	minerals (0.01:20)
Buffer	MES, MOPS, TRIS, CHES (10E-3 M)	no	no	no
Initial concentration (M)	1) 10E-8 M 2) 4.5E-11 M	3.2E-6 M	10E-8 M	$1 \cdot 10^{-10}$ M.
Conditioning time (d)	rocks & minerals (1d)	rocks & minerals (1d)	rocks & minerals (1d)	minerals (1d)
Contact time (d)	rocks (7d) minerals (3d)	rocks (7d) minerals (3d)	rocks (7d) minerals (3d)	minerals (3d)
Tracer isotope	1) ^{93m}Nb 2) ^{95}Nb	^{75}Se	^{233}U	^{234}Th
Carrier (M)	1) yes 2) no	no	no	^{232}Th
Solution	1) reference waters (OLGA, ALLMR, OLBA, OLSR) 2) 0.1 M Na- & Ca-perchlorate	reference waters (OLGA, ALLMR, OLBA, OLSR, OLGO, ALLMO, OLSO)	reference waters (ALLMR, OLSR)	reference waters (OLGA, ALLMR, OLBA, OLSR)
Solid	rocks (T-MGN, P-TGG, T-TGG, PGR) minerals (illite*, kaolinite*)	rocks (T-MGN, P-TGG, T-TGG, PGR) minerals (illite*, kaolinite*)	rocks (P-TGG & PGR) minerals (illite*, kaolinite*)	minerals (illite*, kaolinite*)
Atmosphere	N_2 (MBraun 150MB-GH-B)	1) N_2 (MBraun 150MB-GH-B) 2) ambient atmosphere	N_2 (MBraun 150MB-GH-B)	N_2 (MBraun 150MB-GH-B)
Detection	gamma spectroscopy (Wizard 3" 1480)	gamma spectroscopy (Wizard 3" 1480)	LSC (Quantulus 1220)	LSC (Cerenkov) (Quantulus 1220)
Separation	centrifugation & filtration (0.22µm)	centrifugation & filtration (0.22µm)	centrifugation & filtration (0.22µm)	centrifugation & filtration (0.22µm)
Vessels	polyethylene	polyethylene	polyethylene	polyethylene

*pretreated according to Tournassat et al. 2007.

	Mo	Pa	Sn
pH	5.8-10 (initial & final)	5.8-10 (initial & final)	5.8-10 (initial & final)
S:L(g/mL)	rocks (0.5:20) minerals (0.2:20)	rocks (0.2:20) minerals (0.02:20)	rocks (1:20) minerals (0.05:20)
Buffer	MES, MOPS, TRIS, CHES (10E-3 M)	MES, MOPS, TRIS, CHES (10E-3 M)	MES, MOPS, TRIS, CHES (10E-3 M)
Initial concentration (M)	5E-13 M	4E-11 M	8E-7 M
Conditioning time (d)	rocks & minerals (1d)	rocks & minerals (1d)	rocks & minerals (1d)
Contact time (d)	rocks (7d) minerals (7d)	rocks (7d) minerals (7d)	rocks (7d) minerals (7d)
Tracer isotope	^{99}Mo	^{233}Pa	^{113}Sn
Carrier (M)	yes	no	yes
Solution	reference waters (ALLMR, OLSR)	reference waters (ALLMR, OLSR)	reference waters (ALLMR, OLSR, OLBA, OLGA, OLGO)
Solid	rocks (P-TGG, T-TGG, PGR) minerals (illite*, kaolinite*)	rocks (P-TGG, PGR) minerals (illite*, kaolinite*)	rocks (T-MGN,P-TGG, T-TGG, PGR) minerals (illite*, kaolinite*, chlorite)
Atmosphere	Argon (in-house made glove-box)	Argon (in-house made glove-box)	Argon (in-house made glove-box)
Detection	gamma spectroscopy (Wizard 3" 1480)	gamma spectroscopy (Wizard 3" 1480)	gamma spectroscopy (Wizard 3" 1480)
Separation	centrifugation & filtration (0.22µm)	centrifugation & filtration (0.22µm)	centrifugation & filtration (0.22µm)
Vessels	polyethylene	polyethylene	polyethylene

*pretreated according to Tournassat et al. 2007.

APPENDIX 5 Tables of K_d values

Table A-7. *Best estimate K_d values (m^3/kg) for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	1.4E-04	1.4E-04	5.0E-05	-	5.0E-07	4.0E-09	-	5.0E-06	3.8E-08
Am(III)	1.5E-01	1.5E-01	2.4E+00		3.0E+00	3.0E+00		3.0E+00	3.0E+00
Be(II)	9.2E-01	9.2E-01	3.2E+00		3.2E+00	3.2E+00		3.2E+00	3.2E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	2.0E-04	2.0E-04	6.7E-06		1.7E-06	1.3E-07		1.0E-05	1.0E-06
Cm(III)	1.5E-01	1.5E-01	2.4E+00		3.0E+00	3.0E+00		3.0E+00	3.0E+00
Cs(I)	1.3E+00	1.3E+00	8.4E-01		9.0E-02	8.0E-02		1.2E-01	9.5E-02
Eu(III)	1.5E-01	1.5E-01	2.4E+00		3.0E+00	3.0E+00		3.0E+00	3.0E+00
Ho(III)									
I(-I)	6.0E-04	6.0E-04	2.0E-05		5.0E-06	4.0E-07		3.0E-05	3.0E-06
Mo(VI)	2.6E-03	2.6E-03	2.0E-03		1.5E-03	1.4E-03		2.4E-03	2.3E-03
Nb(V)	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00
Ni(II)	1.5E-02	1.5E-02	2.9E+00	-	1.1E-01	6.0E-01	-	1.5E-01	7.0E-02
Np(IV)	3.0E+00	-	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00
Np(V)		2.0E-05		6.0E-04			6.0E-05		
Pa(V)	2.7E+00	2.7E+00	2.2E+00		1.1E-01	1.0E-01		1.1E-01	1.1E-01
Pd(II)	1.5E-02	1.5E-02	2.9E+00	-	1.1E-01	6.0E-01	-	1.5E-01	7.0E-02
Pu(III)	1.5E-01	-	2.4E+00	-	3.0E+00	3.0E+00	-	3.0E+00	3.0E+00
Pu(IV)	-	-	1.2E+01	-	-	1.2E+01	-	-	-
Pu(V,VI)	-	2.0E-03	-	7.0E-02	-	-	7.0E-02	-	-
Ra(II)	3.5E-01	3.5E-01	1.2E-01	1.2E-01	6.0E-02	2.3E-02	2.3E-02	1.0E-01	4.0E-02
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	7.4E-03	1.8E-03	5.4E-03	1.6E-03	7.9E-03	3.8E-03	1.2E-03	7.9E-03	4.3E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.6E+01	1.6E+01	1.8E+00		1.0E+01	4.0E+00		1.0E+01	1.0E+01
Sr(II)	1.6E-02	1.6E-02	5.4E-03	5.4E-03	6.0E-04	1.2E-05	1.2E-05	2.0E-03	3.0E-05
Tc(IV,VII)	3.0E+00	6.0E-04	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00
Th(IV)	3.0E+00	-	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00
U(IV,VI)	3.0E+00	4.2E-02	4.2E-02	4.2E-02	8.0E-02	8.0E+00	5.4E-02	2.2E-02	8.0E-01
Zr(IV)	3.0E+00	-	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00

Table A-8. *Best estimate K_d values (m^3/kg) for T-MGN Olkiluoto T-series mica gneiss at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	1.4E-04	1.4E-04	5.0E-05	-	5.0E-07	4.0E-09	-	5.0E-06	3.8E-08
Am(III)	3.0E+00	3.0E+00	2.7E+00		2.7E+00	2.7E+00		4.5E-02	2.7E+00
Be(II)	3.2E+00	3.2E+00	3.2E+00		3.2E+00	3.2E+00		3.2E+00	3.2E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, - CO_2H									
Cl(-I)	2.0E-06	2.0E-06	2.0E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	3.0E+00	3.0E+00	2.7E+00		2.7E+00	2.7E+00		4.5E-02	2.7E+00
Cs(I)	1.7E+00	1.7E+00	9.7E-01		1.0E-01	9.0E-02		1.4E-01	1.1E-01
Eu(III)	3.0E+00	3.0E+00	2.7E+00		2.7E+00	2.7E+00		4.5E-02	2.7E+00
Ho(III)									
I(-I)	6.0E-06	6.0E-06	6.0E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.6E-03	1.6E-03	1.6E-03		9.2E-04	9.2E-04		9.2E-04	9.2E-04
Nb(V)	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00	1.9E+00
Ni(II)	5.9E+00	5.9E+00	5.9E+00	-	5.9E+00	5.9E+00	-	5.9E+00	5.9E+00
Np(IV)	8.0E+00	-	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00
Np(V)		2.0E-03		6.0E-04			2.0E-03		
Pa(V)	1.8E+00	1.8E+00	1.8E+00		6.0E-02	6.0E-02		6.0E-02	6.0E-02
Pd(II)	5.9E+00	5.9E+00	5.9E+00	-	5.9E+00	5.9E+00	-	5.9E+00	5.9E+00
Pu(III)	3.0E+00	-	2.7E+00	-	2.7E+00	2.7E+00	-	4.5E-02	2.7E+00
Pu(IV)	1.2E+01	-	1.2E+01	-	1.2E+01	1.2E+01	-	4.0E+00	1.2E+01
Pu(V,VI)	-	2.0E-03	-	6.0E-04	-	-	2.0E-03	-	-
Ra(II)	3.5E-01	3.5E-01	1.2E-01	1.2E-01	6.0E-02	2.3E-02	2.3E-02	1.0E-01	4.0E-02
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	7.6E-04	5.0E-04	1.5E-03	4.6E-04	8.4E-04	1.1E-03	6.7E-04	1.5E-03	1.1E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	3.6E-02	3.6E-02	3.6E-02		3.6E-02	3.6E-02		3.6E-02	3.6E-02
Sr(II)	1.6E-02	1.6E-02	5.4E-03	5.4E-03	6.0E-04	1.2E-05	1.2E-05	2.0E-03	3.0E-05
Tc(IV,VII)	7.8E+00	6.0E-06	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00
Th(IV)	8.0E+00	-	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00
U(IV,VI)	8.0E+00	3.2E-02	3.2E-02	3.2E-02	8.0E+00	8.0E+00	5.4E-02	2.2E-02	8.0E+00
Zr(IV)	8.0E+00	-	8.0E+00	-	8.0E+00	8.0E+00	-	8.0E+00	8.0E+00

Table A-9. *Lower limit K_d values (m^3/kg) for T-MGN Olkiluoto T-series mica gneiss at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	7.0E-06	7.0E-06	2.0E-06	-	2.0E-08	2.0E-10	-	2.0E-07	2.0E-09
Am(III)	7.5E-03	7.5E-03	1.2E-01		1.5E-01	1.5E-01		1.5E-01	1.5E-01
Be(II)	7.5E-04	7.5E-04	1.5E-01		5.5E-03	3.0E-02		7.5E-04	3.5E-03
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	2.9E-05	2.9E-05	9.5E-07		2.4E-07	1.9E-08		1.4E-06	1.4E-07
Cm(III)	7.5E-03	7.5E-03	1.2E-01		1.5E-01	1.5E-01		1.5E-01	1.5E-01
Cs(I)	8.1E-01	8.1E-01	5.5E-01		5.4E-02	4.8E-02		7.3E-02	5.7E-02
Eu(III)	7.5E-03	7.5E-03	1.2E-01		1.5E-01	1.5E-01		1.5E-01	1.5E-01
Ho(III)									
I(-I)	8.6E-05	8.6E-05	2.9E-06		7.1E-07	5.7E-08		4.3E-06	4.3E-07
Mo(VI)	5.2E-04	5.2E-04	4.0E-04		3.0E-04	2.8E-04		4.8E-04	4.6E-04
Nb(V)	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01
Ni(II)	7.5E-04	7.5E-04	1.5E-01	-	5.5E-03	3.0E-02	-	7.5E-03	3.5E-03
Np(IV)	1.5E-01	-	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01
Np(V)		1.0E-06		3.0E-05			3.0E-06		
Pa(V)	5.4E-01	5.4E-01	4.4E-01		2.2E-02	2.0E-02		2.2E-02	2.2E-02
Pd(II)	7.5E-04	7.5E-04	1.5E-01	-	5.5E-03	3.0E-02	-	7.5E-03	3.5E-03
Pu(III)	7.5E-03	-	1.2E-01	-	1.5E-01	1.5E-01	-	1.5E-01	1.5E-01
Pu(IV)	-	-	6.0E-01	-	-	6.0E-01	-	-	-
Pu(V,VI)	-	1.0E-06	-	3.0E-05	-	-	3.0E-06	-	-
Ra(II)	1.8E-02	1.8E-02	6.0E-03	6.0E-03	3.0E-03	1.2E-03	1.2E-03	5.0E-03	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.5E-03	3.6E-04	1.1E-03	3.2E-03	1.6E-03	7.6E-04	2.4E-04	1.6E-03	8.6E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	8.0E-01	8.0E-01	9.0E-02		5.0E-01	2.0E-01		5.0E-01	5.0E-01
Sr(II)	8.0E-04	8.0E-04	2.7E-04	2.7E-04	3.0E-05	6.0E-07	6.0E-07	1.0E-04	1.5E-06
Tc(IV,VII)	1.5E-01	8.6E-05	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01
Th(IV)	1.5E-01	-	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01
U(IV,VI)	6.0E-01	8.4E-03	8.4E-03	8.4E-03	1.6E-02	1.6E+00	1.1E-02	4.4E-03	1.6E-01
Zr(IV)	1.5E-01	-	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01

Table A-10. *Lower limit K_d values (m^3/kg) for T-MGN Olkiluoto T-series mica gneiss at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	7.0E-06	7.0E-06	2.0E-06		2.0E-08	2.0E-10		2.0E-07	2.0E-09
Am(III)	1.5E-01	1.5E-01	1.4E-01		1.4E-01	1.4E-01		2.3E-03	1.4E-01
Be(II)	3.0E-01	3.0E-01	3.0E-01		3.0E-01	3.0E-01		3.0E-01	3.0E-01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, $-CO_2H$									
Cl(-I)	2.9E-07	2.9E-07	2.9E-07		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	1.5E-01	1.5E-01	1.4E-01		1.4E-01	1.4E-01		2.3E-03	1.4E-01
Cs(I)	1.4E+00	1.4E+00	6.3E-01		6.0E-02	6.0E-02		8.0E-02	7.0E-02
Eu(III)	1.5E-01	1.5E-01	1.4E-01		1.4E-01	1.4E-01		2.3E-03	1.4E-01
Ho(III)									
I(-I)	8.6E-06	8.6E-06	6.0E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	3.2E-04	3.2E-04	3.2E-04		1.8E-04	1.8E-04		1.8E-04	1.8E-04
Nb(V)	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01	4.2E-01
Ni(II)	3.0E-01	3.0E-01	3.0E-01	-	3.0E-01	3.0E-01	-	3.0E-01	3.0E-01
Np(IV)	4.0E-01	-	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01
Np(V)		1.0E-04		3.0E-05			1.0E-04		
Pa(V)	3.6E-01	3.6E-01	3.6E-01		1.2E-02	1.2E-02		1.2E-02	1.2E-02
Pd(II)	3.0E-01	3.0E-01	3.0E-01	-	3.0E-01	3.0E-01	-	3.0E-01	3.0E-01
Pu(III)	1.5E-01	-	1.4E-01	-	1.4E-01	1.4E-01	-	2.3E-03	1.4E-01
Pu(IV)	6.0E-01	-	6.0E-01	-	6.0E-01	6.0E-01	-	2.0E-01	6.0E-01
Pu(V,VI)	-	1.0E-04	-	3.0E-05	-	-	1.0E-04	-	-
Ra(II)	1.8E-02	1.8E-02	6.0E-03	6.0E-03	3.0E-03	1.2E-03	1.2E-03	5.0E-03	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.5E-04	1.0E-04	3.0E-04	9.2E-05	1.7E-04	2.2E-04	1.3E-04	3.0E-04	2.2E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.8E-03	1.8E-03	1.8E-03		1.8E-03	1.8E-03		1.8E-03	1.8E-03
Sr(II)	8.0E-04	8.0E-04	2.7E-04	2.7E-04	3.0E-05	6.0E-07	6.0E-07	1.0E-04	1.5E-06
Tc(IV,VII)	3.9E-01	8.6E-06	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01
Th(IV)	4.0E-01	-	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01
U(IV,VI)	1.6E+00	6.4E-03	6.4E-03	6.4E-03	1.6E+00	1.6E+00	1.1E-02	4.4E-03	1.6E+00
Zr(IV)	4.0E-01	-	4.0E-01	-	4.0E-01	4.0E-01	-	4.0E-01	4.0E-01

Table A-11. *Best estimate K_d values (m^3/kg) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	7.0E-05	7.0E-05	2.5E-05	-	2.5E-07	2.0E-09	-	2.5E-06	1.4E-08
Am(III)	7.0E-02	7.0E-02	9.0E-01		1.1E+00	1.1E+00		1.1E+00	1.1E+00
Be(II)	4.4E-01	1.5E+00	1.5E+00		1.5E+00	1.5E+00		1.5E+00	1.5E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.0E-04	1.0E-04	3.3E-06		8.3E-07	6.7E-08		5.0E-06	5.0E-07
Cm(III)	7.0E-02	7.0E-02	9.0E-01		1.1E+00	1.1E+00		1.1E+00	1.1E+00
Cs(I)	6.0E-01	6.0E-01	4.2E-01		4.5E-02	4.0E-02		7.0E-02	5.5E-02
Eu(III)	7.0E-02	7.0E-02	9.0E-01		1.1E+00	1.1E+00		1.1E+00	1.1E+00
Ho(III)									
I(-I)	3.0E-04	3.0E-04	1.0E-05		2.5E-06	2.0E-07		1.5E-05	1.5E-06
Mo(VI)	1.3E-03	1.3E-03	1.0E-03		8.0E-04	7.0E-04		1.2E-03	8.0E-04
Nb(V)	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01
Ni(II)	7.5E-03	7.5E-03	1.5E+00	-	5.5E-02	3.0E-01	-	7.5E-02	3.5E-02
Np(IV)	1.5E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Np(V)		1.0E-05		3.0E-04			3.0E-05		
Pa(V)	1.4E+00	1.4E+00	1.1E+00		6.0E-02	5.0E-02		6.0E-02	6.0E-02
Pd(II)	7.5E-03	7.5E-03	1.5E+00	-	5.5E-02	3.0E-01	-	7.5E-02	3.5E-02
Pu(III)	7.0E-02	-	9.0E-01	-	1.1E+00	1.1E+00	-	1.1E+00	1.1E+00
Pu(IV)	-	-	6.0E+00	-	-	6.0E+00	-	-	-
Pu(V,VI)	-	1.0E-03	-	2.0E-02	-	-	2.0E-02	-	-
Ra(II)	1.7E-01	1.7E-01	6.0E-02	6.0E-02	3.0E-02	1.2E-02	1.2E-02	5.0E-02	2.0E-02
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	2.3E-03	7.0E-04	2.6E-03	6.0E-04	3.4E-03	2.6E-03	4.9E-04	4.0E-03	3.0E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	8.0E+00	8.0E+00	9.0E-01		5.0E-01	2.0E+00		5.0E+00	5.0E+00
Sr(II)	8.0E-03	8.0E-03	2.6E-03	2.6E-03	3.0E-04	6.0E-06	6.0E-06	1.0E-03	1.5E-05
Tc(IV,VII)	1.5E+00	3.0E-04	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Th(IV)	1.5E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
U(IV,VI)	1.5E+00	2.1E-02	2.1E-02	2.1E-02	4.0E-02	4.0E+00	3.5E-02	1.4E-02	4.0E-01
Zr(IV)	1.5E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00

Table A-12. *Best estimate K_d values (m^3/kg) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	7.0E-05	7.0E-05	2.5E-05	-	2.5E-07	2.0E-09	-	2.5E-06	1.4E-08
Am(III)	1.1E+00	1.1E+00	1.0E+00		1.0E+00	1.0E+00		1.5E-02	1.0E+00
Be(II)	1.5E+00	1.5E+00	1.5E+00		1.5E+00	1.5E+00		1.5E+00	1.5E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.0E-06	1.0E-06	1.0E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	1.1E+00	1.1E+00	1.0E+00		1.0E+00	1.0E+00		1.5E-02	1.0E+00
Cs(I)	8.0E-01	8.0E-01	4.8E-01		5.0E-02	4.5E-02		7.0E-02	5.5E-02
Eu(III)	1.1E+00	1.1E+00	1.0E+00		1.0E+00	1.0E+00		1.5E-02	1.0E+00
Ho(III)									
I(-I)	3.0E-06	3.0E-06	3.0E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	0.8E-03	0.8E-03	0.8E-03		4.4E-04	4.4E-04		4.4E-04	4.4E-04
Nb(V)	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01	2.9E-01
Ni(II)	3.0E+00	3.0E+00	3.0E+00	-	3.0E+00	3.0E+00	-	3.0E+00	3.0E+00
Np(IV)	4.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Np(V)		1.0E-03		3.0E-04			1.0E-03		
Pa(V)	9.0E-01	9.0E-01	9.0E-01		3.0E-02	3.0E-02		3.0E-02	3.0E-02
Pd(II)	3.0E+00	3.0E+00	3.0E+00	-	3.0E+00	3.0E+00	-	3.0E+00	3.0E+00
Pu(III)	1.1E+00	-	1.1E+00	-	1.1E+00	1.1E+00	-	1.5E-02	1.1E+00
Pu(IV)	6.0E+00	-	6.0E+00	-	6.0E+00	6.0E+00	-	2.0E+00	6.0E+00
Pu(V,VI)	-	1.0E-03	-	3.0E-04	-	-	1.0E-03	-	-
Ra(II)	1.7E-02	1.7E-02	6.0E-02	6.0E-02	3.0E-02	1.2E-02	1.2E-02	5.0E-02	2.0E-02
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.2E-03	2.8E-04	4.1E-04	2.2E-04	1.4E-04	3.5E-04	2.8E-04	4.1E-04	3.5E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.8E-02	1.8E-02	1.8E-02		1.8E-02	1.8E-02		1.8E-02	1.8E-02
Sr(II)	8.0E-03	8.0E-03	2.6E-03	2.6E-03	3.0E-04	6.0E-06	6.0E-06	1.0E-03	1.5E-05
Tc(IV,VII)	3.9E+00	3.0E-06	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Th(IV)	4.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
U(IV,VI)	4.0E+00	2.1E-02	2.1E-02	2.1E-02	4.0E+00	4.0E+00	3.5E-02	1.4E-02	4.0E+00
Zr(IV)	4.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00

Table A-13. *Lower limit K_d values (m^3/kg) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	3.5E-06	3.5E-06	1.0E-06	-	1.0E-08	1.0E-10	-	1.0E-07	1.0E-09
Am(III)	3.5E-03	3.5E-03	4.5E-02	5.5E-02	5.5E-02			5.5E-02	5.5E-02
Be(II)	3.8E-04	3.8E-04	7.5E-02		2.8E-03	1.5E-02		3.8E-03	1.8E-03
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.4E-05	1.4E-05	4.8E-07		1.2E-07	9.5E-09		7.1E-07	7.1E-08
Cm(III)	3.5E-03	3.5E-03	4.5E-02	5.5E-02	5.5E-02			5.5E-02	5.5E-02
Cs(I)	4.1E-01	4.1E-01	2.8E-01		2.7E-02	2.4E-02		3.7E-02	2.9E-02
Eu(III)	3.5E-03	3.5E-03	4.5E-02	5.5E-02	5.5E-02			5.5E-02	5.5E-02
Ho(III)									
I(-I)	4.3E-05	4.3E-05	1.4E-06		3.6E-07	2.9E-08		2.1E-06	2.1E-07
Mo(VI)	2.6E-04	2.6E-04	2.0E-04		1.6E-04	1.4E-04		2.4E-04	1.6E-04
Nb(V)	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02
Ni(II)	3.8E-04	3.8E-04	7.5E-02	-	2.8E-03	1.5E-02	-	3.8E-03	1.8E-03
Np(IV)	7.5E-02	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Np(V)		5.0E-07		2.0E-05			2.0E-06		
Pa(V)	2.8E-01	2.8E-01	2.2E-01		1.2E-02	1.0E-02		1.2E-02	1.2E-02
Pd(II)	3.8E-04	3.8E-04	7.5E-02	-	2.8E-03	1.5E-02	-	3.8E-03	1.8E-03
Pu(III)	3.5E-03	-	4.5E-02	-	5.5E-02	5.5E-02	-	5.5E-02	5.5E-02
Pu(IV)	-	-	3.0E-01	-	-	3.0E-01	-	-	-
Pu(V,VI)	-	5.0E-07	-	2.0E-05	-	-	2.0E-06	-	-
Ra(II)	9.0E-03	9.0E-03	3.0E-03	3.0E-03	1.5E-03	6.0E-04	6.0E-04	2.5E-03	1.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	4.6E-04	1.4E-04	5.2E-04	1.2E-04	6.8E-04	5.2E-04	9.8E-05	8.0E-04	6.0E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	4.0E-01	4.0E-01	4.5E-02		2.5E-02	1.0E-01		2.5E-01	3.0E-01
Sr(II)	4.0E-04	4.0E-04	1.8E-04	1.8E-04	1.5E-05	3.0E-07	3.0E-07	5.0E-05	7.0E-07
Tc(IV,VII)	7.5E-02	4.3E-05	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Th(IV)	7.5E-02	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
U(IV,VI)	3.0E-01	4.2E-03	4.2E-03	4.2E-03	8.0E-03	8.0E-01	7.0E-03	2.8E-03	8.0E-02
Zr(IV)	7.5E-02	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01

Table A-14. *Lower limit K_d values (m^3/kg) for P-TGG Olkiluoto P-series tonalite granodiorite granite gneiss at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	3.5E-06	3.5E-06	1.0E-06	-	1.0E-08	1.0E-10	-	1.0E-07	1.0E-09
Am(III)	5.5E-02	5.5E-02	5.0E-02		5.0E-02	5.0E-02		7.5E-04	5.0E-02
Be(II)	1.5E-01	1.5E-01	1.5E-01		1.5E-01	1.5E-01		1.5E-01	1.5E-01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.4E-07	1.4E-07	1.4E-07		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	5.5E-02	5.5E-02	5.0E-02		5.0E-02	5.0E-02		7.5E-04	5.0E-02
Cs(I)	5.3E-01	5.3E-01	3.2E-01		3.0E-02	3.0E-02		4.0E-02	3.5E-02
Eu(III)	5.5E-02	5.5E-02	5.0E-02		5.0E-02	5.0E-02		7.5E-04	5.0E-02
Ho(III)									
I(-I)	1.5E-07	1.5E-07	1.5E-07		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.6E-04	1.6E-04	1.6E-04		8.8E-05	8.8E-05		8.8E-05	8.8E-05
Nb(V)	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02	5.8E-02
Ni(II)	1.5E-01	1.5E-01	1.5E-01	-	1.5E-01	1.5E-01	-	1.5E-01	1.5E-01
Np(IV)	2.0E-01	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Np(V)		5.0E-05		2.0E-05			5.0E-05		
Pa(V)	1.8E-01	1.8E-01	1.8E-01		6.0E-03	6.0E-03		6.0E-03	6.0E-03
Pd(II)	1.5E-01	1.5E-01	1.5E-01	-	1.5E-01	1.5E-01	-	1.5E-01	1.5E-01
Pu(III)	5.5E-02	-	5.0E-02	-	5.0E-02	5.0E-02	-	7.5E-04	5.0E-02
Pu(IV)	3.0E-01	-	3.0E-01	-	3.0E-01	3.0E-01	-	1.0E-01	3.0E-01
Pu(V,VI)	-	5.0E-05	-	2.0E-05	-	-	5.0E-05	-	-
Ra(II)	9.0E-04	9.0E-04	3.0E-03	3.0E-03	1.5E-03	6.0E-04	6.0E-04	2.5E-03	1.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	2.4E-04	5.6E-05	8.2E-05	4.4E-05	2.8E-05	7.0E-05	5.6E-05	8.2E-05	7.0E-05
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	9.0E-04	9.0E-04	9.0E-04		9.0E-04	9.0E-04		9.0E-04	9.0E-04
Sr(II)	4.0E-04	4.0E-04	1.8E-04	1.8E-04	1.5E-05	3.0E-07	3.0E-07	5.0E-05	7.0E-07
Tc(IV,VII)	2.0E-01	1.5E-07	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Th(IV)	2.0E-01	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
U(IV,VI)	8.0E-01	4.2E-03	4.2E-03	4.2E-03	8.0E-01	8.0E-01	7.0E-03	2.8E-03	8.0E-01
Zr(IV)	2.0E-01	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01

Table A-15. *Best estimate K_d values (m^3/kg) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	6.0E-05	6.0E-05	2.0E-05	-	2.0E-07	2.0E-09	-	2.0E-06	2.0E-08
Am(III)	3.0E-02	3.0E-02	5.0E-01		5.8E-01	5.8E-01		5.8E-01	5.8E-01
Be(II)	4.0E-01	4.0E-01	1.4E+00		1.4E+00	1.4E+00		1.4E+00	1.4E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	6.7E-05	6.7E-05	1.7E-06		3.3E-07	2.0E-08		3.0E-06	5.0E-08
Cm(III)	3.0E-02	3.0E-02	5.0E-01		5.8E-01	5.8E-01		5.8E-01	5.8E-01
Cs(I)	4.8E-01	4.8E-01	3.2E-01		3.5E-02	3.0E-02		4.6E-02	3.7E-02
Eu(III)	3.0E-02	3.0E-02	5.0E-01		5.8E-01	5.8E-01		5.8E-01	5.8E-01
Ho(III)									
I(-I)	2.0E-04	2.0E-04	5.0E-06		1.0E-06	6.0E-08		9.0E-06	1.5E-07
Mo(VI)	8.6E-04	8.6E-04	5.0E-04		5.0E-04	3.6E-04		7.2E-04	5.4E-04
Nb(V)	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01
Ni(II)	6.5E-03	6.5E-03	1.3E+00	-	7.0E-02	2.6E-01	-	8.0E-02	2.9E-02
Np(IV)	1.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	--	4.0E+00	4.0E+00
Np(V)		8.0E-06		3.0E-04			3.0E-05		
Pa(V)	1.2E+00	1.2E+00	1.0E+00		5.1E-02	4.3E-02		5.1E-02	4.3E-02
Pd(II)	6.5E-03	6.5E-03	1.3E+00	-	7.0E-02	2.6E-01	-	8.0E-02	2.9E-02
Pu(III)	3.0E-02	-	5.0E-01	-	5.8E-01	5.8E-01	-	5.8E-01	5.8E-01
Pu(IV)	-	-	2.5E+00	-	-	2.5E+00	-	-	-
Pu(V,VI)	-	5.0E-04	-	2.0E-02	-	-	2.0E-02	-	-
Ra(II)	1.4E-01	1.4E-01	4.6E-02	4.6E-02	3.0E-02	9.1E-03	9.1E-03	4.0E-02	4.0E-02
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	4.0E-04	6.0E-04	9.2E-04	3.2E-04	1.2E-03	5.7E-04	4.5E-04	1.4E-03	6.4E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	7.0E+00	7.0E+00	7.0E-01		5.0E+00	1.9E+00		4.1E+00	5.0E+00
Sr(II)	6.1E-03	6.1E-03	2.0E-03	2.0E-03	2.0E-04	4.6E-06	4.6E-06	1.0E-03	1.0E-05
Tc(IV,VII)	1.0E+00	2.0E-04	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Th(IV)	1.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
U(IV,VI)	1.0E+00	6.8E-03	6.8E-03	6.8E-03	4.0E-02	4.0E+00	2.5E-02	4.7E-03	4.0E-01
Zr(IV)	1.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00

Table A-16. *Best estimate K_d values (m^3/kg) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	6.0E-05	6.0E-05	2.0E-05	-	2.0E-07	2.0E-09	-	2.0E-06	2.0E-08
Am(III)	6.0E-01	6.0E-01	5.0E-01		5.0E-01	5.0E-01		8.0E-03	5.0E-01
Be(II)	1.4E+00	1.4E+00	1.4E+00		1.4E+00	1.4E+00		1.4E+00	1.4E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	3.3E-07	3.3E-07	3.3E-07		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	6.0E-01	6.0E-01	5.0E-01		5.0E-01	5.0E-01		8.0E-03	5.0E-01
Cs(I)	6.0E-01	6.0E-10	3.7E-01	4.0E-02	3.5E-02	5.0E-02	4.3E-02		
Eu(III)	6.0E-01	6.0E-01	5.0E-01		5.0E-01	5.0E-01		8.0E-03	5.0E-01
Ho(III)									
I(-I)	1.0E-06	1.0E-06	1.0E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	2.4E-04	2.4E-04	2.4E-04		1.0E-05	1.0E-05		1.0E-05	1.0E-05
Nb(V)	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01	3.2E-01
Ni(II)	2.6E+00	2.6E+00	2.6E+00	-	2.6E+00	2.6E+00	-	2.6E+00	2.6E+00
Np(IV)	4.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Np(V)		1.0E-03		3.0E-04	1.0E-03		1.0E-03		
Pa(V)	8.4E-01	8.4E-01	8.4E-01		2.5E-02	2.5E-02		2.5E-02	2.5E-02
Pd(II)	2.6E+00	2.6E+00	2.6E+00	-	2.6E+00	2.6E+00	-	2.6E+00	2.6E+00
Pu(III)	6.0E-01	-	5.0E-01	-	5.0E-01	5.0E-01	-	8.0E-03	5.0E-01
Pu(IV)	2.5E+00	-	2.5E+00	-	2.5E+00	2.5E+00	-	8.0E-01	2.5E+00
Pu(V,VI)	-	1.0E-03	-	3.0E-04	-	-	1.0E-03	-	-
Ra(II)	1.4E-01	1.4E-01	4.6E-02	4.6E-02	3.0E-02	9.1E-03	9.1E-03	4.0E-02	4.0E-02
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	3.1E-04	1.5E-04	2.2E-04	1.2E-04	6.8E-05	1.8E-04	2.3E-04	2.2E-04	1.8E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.7E-02	1.7E-02	1.7E-02		1.7E-02	1.7E-02		1.7E-02	1.7E-02
Sr(II)	6.1E-03	6.1E-03	2.0E-03	2.0E-03	2.0E-04	4.6E-06	4.6E-06	1.0E-03	1.0E-05
Tc(IV,VII)	3.9E+00	1.0E-06	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
Th(IV)	4.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00
U(IV,VI)	4.0E+00	6.8E-03	6.8E-03	6.8E-03	4.0E+00	4.0E+00	2.5E-02	4.7E-03	4.0E+00
Zr(IV)	4.0E+00	-	4.0E+00	-	4.0E+00	4.0E+00	-	4.0E+00	4.0E+00

Table A-17. *Lower limit K_d values (m^3/kg) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	2.0E-06	2.0E-06	1.0E-06	-	1.0E-08	1.0E-10	-	1.0E-07	1.0E-09
Am(III)	1.5E-03	1.5E-03	2.5E-02		2.9E-02	2.9E-02		2.9E-02	2.9E-02
Be(II)	3.3E-04	3.3E-04	6.5E-02		3.5E-03	1.3E-02		4.0E-03	1.5E-03
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	3.3E-06	3.3E-06	8.3E-08		1.7E-08	1.0E-09		1.5E-07	2.5E-09
Cm(III)	1.5E-03	1.5E-03	2.5E-02		2.9E-02	2.9E-02		2.9E-02	2.9E-02
Cs(I)	4.0E-02	4.0E-02	3.0E-02		3.0E-03	2.6E-03		4.0E-03	3.0E-03
Eu(III)	1.5E-03	1.5E-03	2.5E-02		2.9E-02	2.9E-02		2.9E-02	2.9E-02
Ho(III)									
I(-I)	1.0E-05	1.0E-05	2.5E-07		5.0E-08	3.0E-09		4.5E-07	7.5E-09
Mo(VI)	4.3E-05	4.3E-05	2.5E-05		2.5E-05	1.8E-05		3.6E-05	2.7E-05
Nb(V)	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02
Ni(II)	3.3E-04	3.3E-04	6.5E-02	-	3.5E-03	1.3E-02	-	4.0E-03	1.5E-03
Np(IV)	5.0E-02	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Np(V)		4.0E-07		2.0E-05			4.0E-05		
Pa(V)	6.0E-02	6.0E-02	5.0E-02		2.6E-03	2.2E-03		2.6E-03	2.2E-03
Pd(II)	3.3E-04	3.3E-04	6.5E-02	-	3.5E-03	1.3E-02	-	4.0E-03	1.5E-03
Pu(III)	1.5E-03	-	2.5E-02	-	2.9E-02	2.9E-02	-	2.9E-02	2.9E-02
Pu(IV)	-	-	1.3E-01	-	-	1.3E-01	-	-	-
Pu(V,VI)	-	4.0E-07	-	2.0E-05	-	-	4.0E-05	-	-
Ra(II)	7.0E-03	7.0E-03	2.3E-03	2.3E-03	1.5E-03	4.6E-04	4.6E-04	2.0E-03	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	2.0E-05	3.0E-04	4.6E-05	1.6E-05	6.0E-05	2.9E-05	2.3E-05	7.0E-05	3.2E-05
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	3.5E-01	3.5E-01	3.5E-02		2.5E-01	9.5E-02		2.1E-01	3.0E-01
Sr(II)	3.1E-04	3.1E-04	1.0E-04	1.0E-04	1.0E-05	2.3E-07	2.3E-07	5.0E-05	5.0E-07
Tc(IV,VII)	5.0E-02	1.0E-05	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Th(IV)	5.0E-02	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
U(IV,VI)	5.0E-02	3.3E-04	3.3E-04	3.3E-04	2.0E-03	2.0E-01	1.3E-03	2.4E-04	2.0E-02
Zr(IV)	5.0E-02	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01

Table A-18. *Lower limit K_d values (m^3/kg) for T-TGG Olkiluoto T-series tonalite granodiorite granite gneiss at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	2.0E-06	2.0E-06	1.0E-06	-	1.0E-08	1.0E-10	-	1.0E-07	1.0E-09
Am(III)	3.0E-02	3.0E-02	2.5E-02		2.5E-02	2.5E-02		4.0E-04	2.5E-02
Be(II)	1.3E-01	1.3E-01	1.3E-01		1.3E-01	1.3E-01		1.3E-01	1.3E-01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.7E-08	1.7E-08	1.7E-08		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	3.0E-02	3.0E-02	2.5E-02		2.5E-02	2.5E-02		4.0E-04	2.5E-02
Cs(I)	5.2E-02	5.2E-02	3.0E-02		3.0E-03	3.0E-03		4.0E-03	3.0E-03
Eu(III)	3.0E-02	3.0E-02	2.5E-02		2.5E-02	2.5E-02		4.0E-04	2.5E-02
Ho(III)									
I(-I)	5.0E-08	5.0E-08	5.0E-08		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.2E-05	1.2E-05	1.2E-05		5.0E-07	5.0E-07		5.0E-07	5.0E-07
Nb(V)	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02
Ni(II)	1.3E-01	1.3E-01	1.3E-01	-	1.3E-01	1.3E-01	-	1.3E-01	1.3E-01
Np(IV)	2.0E-01	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Np(V)		4.0E-05		2.0E-05			2.0E-06		
Pa(V)	4.2E-02	4.2E-02	4.2E-02		1.3E-03	1.3E-03		1.3E-03	1.3E-03
Pd(II)	1.3E-01	1.3E-01	1.3E-01	-	1.3E-01	1.3E-01	-	1.3E-01	1.3E-01
Pu(III)	3.0E-02	-	2.5E-02	-	2.5E-02	2.5E-02	-	4.0E-04	2.5E-02
Pu(IV)	1.3E-01	-	1.3E-01	-	1.3E-01	1.3E-01	-	4.0E-02	1.3E-01
Pu(V,VI)	-	4.0E-05	-	2.0E-05	-	-	2.0E-06	-	-
Ra(II)	7.0E-03	7.0E-03	2.3E-03	2.3E-03	1.5E-03	4.6E-04	4.6E-04	2.0E-03	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.6E-05	7.5E-06	1.1E-05	6.0E-06	3.4E-06	9.0E-06	1.2E-05	1.1E-05	9.0E-06
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	8.5E-04	8.5E-04	8.5E-04		8.5E-04	8.5E-04		8.5E-04	8.5E-04
Sr(II)	3.1E-04	3.1E-04	1.0E-04	1.0E-04	1.0E-05	2.3E-07	2.3E-07	5.0E-05	5.0E-07
Tc(IV,VII)	2.0E-01	5.0E-08	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
Th(IV)	2.0E-01	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01
U(IV,VI)	2.0E-01	3.3E-04	3.3E-04	3.3E-04	2.0E-01	2.0E-01	1.3E-03	2.4E-04	2.0E-01
Zr(IV)	2.0E-01	-	2.0E-01	-	2.0E-01	2.0E-01	-	2.0E-01	2.0E-01

Table A-19. *Best estimate K_d values (m^3/kg) for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	6.0E-06	6.0E-06	2.0E-06	-	2.0E-08	2.0E-10	-	2.0E-07	2.0E-09
Am(III)	6.0E-03	6.0E-03	9.0E-02		1.1E-01	1.1E-01		1.1E-01	1.1E-01
Be(II)	1.9E-01	6.4E-01	6.4E-01	6.4E-01	6.4E-01	6.4E-01		6.4E	01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.3E-05	1.3E-05	3.3E-07		1.0E-07	6.7E-09		6.7E-07	6.7E-08
Cm(III)	6.0E-03	6.0E-03	9.0E-02		1.1E-01	1.1E-01		1.1E-01	1.1E-01
Cs(I)	5.0E-02	5.0E-02	3.5E-02		4.0E-03	3.0E-03		5.0E-03	4.0E-03
Eu(III)	6.0E-03	6.0E-03	9.0E-02		1.1E-01	1.1E-01		1.1E-01	1.1E-01
Ho(III)									
I(-I)	4.0E-05	4.0E-05	1.0E-06		3.0E-07	2.0E-08		2.0E-06	2.0E-07
Mo(VI)	1.7E-04	1.7E-04	7.7E-05		3.4E-06	2.4E-06		1.3E-04	4.1E-06
Nb(V)	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01
Ni(II)	2.6E-03	2.6E-03	5.1E-01	-	2.0E-02	3.5E-01	-	3.0E-02	1.2E-02
Np(IV)	3.0E-01	-	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00
Np(V)		4.0E-06		1.0E-04			1.0E-05		
Pa(V)	6.2E-01	6.2E-01	4.4E-01		1.7E-02	1.7E-02		1.7E-02	1.7E-02
Pd(II)	2.6E-03	2.6E-03	5.1E-01	-	2.0E-02	3.5E-01	-	3.0E-02	1.2E-02
Pu(III)	6.0E-03	-	9.0E-02	-	1.1E-01	1.1E-01	-	1.1E-01	1.1E-01
Pu(IV)	-	-	1.0E+00	-	-	1.0E+00	-	-	-
Pu(V,VI)	-	1.0E-04	-	3.0E-03	-	-	3.0E-03	-	-
Ra(II)	1.5E-02	1.5E-02	5.0E-03	5.0E-03	3.0E-03	1.1E-03	1.1E-03	4.0E-03	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.4E-04	1.2E-04	2.0E-04	1.2E-04	8.8E-04	2.7E-04	1.9E-04	2.6E-04	3.0E-04
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	2.8E+00	2.8E+00	3.0E-01		2.0E+00	7.0E-01		1.8E+00	2.1E+00
Sr(II)	6.7E-04	6.7E-04	2.2E-04	2.2E-04	2.0E-05	5.0E-07	5.0E-07	1.0E-04	1.0E-06
Tc(IV,VII)	3.0E-01	4.0E-05	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00
Th(IV)	3.0E-01	-	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00
U(IV,VI)	3.0E-01	2.8E-03	2.8E-03	2.8E-03	1.0E-02	1.0E+00	1.0E-02	1.9E-03	1.0E-01
Zr(IV)	3.0E-01	-	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00

Table A-20. *Best estimate K_d values (m^3/kg) for PGR Olkiluoto pegmatitic granite at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	6.0E-06	6.0E-06	2.0E-06	-	2.0E-08	2.0E-10	-	2.0E-07	2.0E-09
Am(III)	1.0E-01	1.0E-01	1.0E-01		1.0E-01	1.0E-01		1.5E-03	1.0E-01
Be(II)	6.4E-01	6.4E-01	6.4E-01		6.4E-01	6.4E-01		6.4E-01	6.4E-01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	9.0E-08	9.0E-08	9.0E-08		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	1.0E-01	1.0E-01	1.0E-01		1.0E-01	1.0E-01		1.5E-03	1.0E-01
Cs(I)	6.2E-02	6.2E-02	4.0E-02		5.0E-03	3.0E-03		6.0E-03	5.0E-03
Eu(III)	1.0E-01	1.0E-01	1.0E-01		1.0E-01	1.0E-01		1.5E-03	1.0E-01
Ho(III)									
I(-I)	2.7E-07	2.7E-07	2.7E-07		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	9.4E-06	9.4E-06	9.4E-06		4.7E-07	4.7E-07		4.7E-07	4.7E-07
Nb(V)	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01	2.4E-01
Ni(II)	1.1E+00	1.1E+00	1.1E+00	-	1.1E+00	1.1E+00	-	1.1E+00	1.1E+00
Np(IV)	1.0E+00	-	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00
Np(V)		4.0E-04		1.0E-04			4.0E-04		
Pa(V)	3.1E-01	3.1E-01	3.1E-01		1.7E-02	1.7E-02		1.7E-02	1.7E-02
Pd(II)	1.1E+00	1.1E+00	1.1E+00	-	1.1E+00	1.1E+00	-	1.1E+00	1.1E+00
Pu(III)	1.0E-01	-	1.0E-01	-	1.0E-01	1.0E-01	-	1.5E-03	1.0E-01
Pu(IV)	1.0E+00	-	1.0E+00	-	1.0E+00	1.0E+00	-	3.0E-01	1.0E+00
Pu(V,VI)	-	4.0E-04	-	1.0E-04	-	-	4.0E-04	-	-
Ra(II)	1.5E-02	1.5E-02	5.0E-03	5.0E-03	3.0E-03	1.1E-03	1.1E-03	4.0E-03	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	9.7E-05	6.1E-05	1.0E-04	5.1E-05	3.6E-05	8.8E-05	1.4E-04	1.0E-04	8.8E-05
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	7.0E-03	7.0E-03	7.0E-03		7.0E-03	7.0E-03		7.0E-03	7.0E-03
Sr(II)	6.7E-04	6.7E-04	2.2E-04	2.2E-04	2.0E-05	5.0E-07	5.0E-07	1.0E-04	1.0E-06
Tc(IV,VII)	9.8E-01	2.7E-07	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00
Th(IV)	1.0E+00	-	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00
U(IV,VI)	1.0E+00	2.8E-03	2.8E-03	2.8E-03	1.0E+00	1.0E+00	1.0E-02	1.9E-03	1.0E+00
Zr(IV)	1.0E+00	-	1.0E+00	-	1.0E+00	1.0E+00	-	1.0E+00	1.0E+00

Table A-21. *Lower limit K_d values (m^3/kg) for PGR Olkiluoto pegmatitic granite at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	1.0E-07	1.0E-07	4.0E-08	-	4.0E-10	4.0E-12	-	4.0E-09	4.0E-11
Am(III)	1.2E-04	1.2E-04	1.8E-03		2.2E-03	2.2E-03		2.2E-03	2.2E-03
Be(II)	5.2E-05	5.2E-05	1.0E-02		4.0E-04	7.0E-03		6.0E-04	2.4E-04
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	2.7E-07	2.7E-07	6.7E-09		2.0E-09	1.3E-10		1.3E-08	1.3E-09
Cm(III)	1.2E-04	1.2E-04	1.8E-03		2.2E-03	2.2E-03		2.2E-03	2.2E-03
Cs(I)	6.0E-03	6.0E-03	4.0E-03		4.0E-04	3.0E-04		6.0E-04	4.0E-04
Eu(III)	1.2E-04	1.2E-04	1.8E-03		2.2E-03	2.2E-03		2.2E-03	2.2E-03
Ho(III)									
I(-I)	8.0E-07	8.0E-07	2.0E-08		6.0E-09	4.0E-10		4.0E-08	4.0E-09
Mo(VI)	3.4E-06	3.4E-06	1.5E-06		6.8E-08	4.8E-08		2.6E-06	8.2E-08
Nb(V)	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02
Ni(II)	5.2E-05	5.2E-05	1.0E-02	-	4.0E-04	7.0E-03	-	6.0E-04	2.4E-04
Np(IV)	6.0E-03	-	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02
Np(V)		2.0E-08		2.0E-06			2.0E-07		
Pa(V)	1.2E-02	1.2E-02	8.8E-03		3.4E-04	3.4E-04		3.4E-04	3.4E-04
Pd(II)	5.2E-05	5.2E-05	1.0E-02	-	4.0E-04	7.0E-03	-	6.0E-04	2.4E-04
Pu(III)	1.2E-04	-	1.8E-03	-	2.2E-03	2.2E-03	-	2.2E-03	2.2E-03
Pu(IV)	-	-	5.0E-02	-	-	5.0E-02	-	-	-
Pu(V,VI)	-	2.0E-08	-	2.0E-06	-	-	2.0E-07	-	-
Ra(II)	3.0E-04	3.0E-04	1.0E-04	1.0E-04	6.0E-05	2.2E-05	2.2E-05	8.0E-05	8.0E-04
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	2.8E-06	2.8E-06	4.0E-06	2.4E-06	1.8E-05	5.4E-06	3.8E-06	5.2E-06	6.0E-06
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	5.6E-02	5.6E-02	6.0E-03		4.0E-02	1.4E-02		3.6E-02	4.2E-02
Sr(II)	1.3E-05	1.3E-05	4.4E-06	4.4E-06	4.0E-07	1.0E-08	1.0E-08	2.0E-06	2.0E-08
Tc(IV,VII)	6.0E-03	8.0E-07	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02
Th(IV)	6.0E-03	-	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02
U(IV,VI)	6.0E-03	5.6E-05	5.6E-05	5.6E-05	2.0E-4	2.0E-02	2.0E-04	3.8E-05	2.0E-03
Zr(IV)	6.0E-03	-	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02

Table A-22. *Lower limit K_d values (m^3/kg) for PGR Olkiluoto pegmatitic granite at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	1.0E-07	1.0E-07	4.0E-08	-	4.0E-10	4.0E-12	-	4.0E-09	4.0E-11
Am(III)	2.0E-03	2.0E-03	2.0E-03		2.0E-03	2.0E-03		3.0E-05	2.0E-03
Be(II)	2.2E-02	2.2E-02	2.2E-02		2.2E-02	2.2E-02		2.2E-02	2.2E-02
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.8E-09	1.8E-09	1.8E-09		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	2.0E-03	2.0E-03	2.0E-03		2.0E-03	2.0E-03		3.0E-05	2.0E-03
Cs(I)	7.8E-03	7.8E-03	5.0E-03		5.0E-04	4.0E-04		5.0E-04	4.0E-04
Eu(III)	2.0E-03	2.0E-03	2.0E-03		2.0E-03	2.0E-03		3.0E-05	2.0E-03
Ho(III)									
I(-I)	5.4E-09	5.4E-09	5.4E-09		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.9E-07	1.9E-07	1.9E-07		9.4E-09	9.4E-09		9.4E-09	9.4E-09
Nb(V)	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02
Ni(II)	2.2E-02	2.2E-02	2.2E-02	-	2.2E-02	2.2E-02	-	2.2E-02	2.2E-02
Np(IV)	2.0E-02	-	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02
Np(V)		2.0E-06		2.0E-06			2.0E-06		
Pa(V)	6.2E-03	6.2E-03	6.2E-03		3.4E-04	3.4E-04		3.4E-04	3.4E-04
Pd(II)	2.2E-02	2.2E-02	2.2E-02	-	2.2E-02	2.2E-02	-	2.2E-02	2.2E-02
Pu(III)	2.0E-03	-	2.0E-03	-	2.0E-03	2.0E-03	-	3.0E-05	2.0E-03
Pu(IV)	5.0E-02	-	5.0E-02	-	5.0E-02	5.0E-02	-	6.0E-03	5.0E-02
Pu(V,VI)	-	2.0E-06	-	2.0E-06	-	-	2.0E-06	-	-
Ra(II)	3.0E-04	3.0E-04	1.0E-04	1.0E-04	6.0E-05	2.2E-05	2.2E-05	8.0E-05	8.0E-04
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.9E-06	1.2E-06	2.0E-06	1.0E-06	7.2E-07	1.8E-06	2.8E-06	2.0E-06	1.8E-06
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.4E-04	1.4E-04	1.4E-04		1.4E-04	1.4E-04		1.4E-04	1.4E-04
Sr(II)	1.3E-05	1.3E-05	4.4E-06	4.4E-06	4.0E-07	1.0E-08	1.0E-08	2.0E-06	2.0E-08
Tc(IV,VII)	2.0E-02	5.4E-09	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02
Th(IV)	2.0E-02	-	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02
U(IV,VI)	2.0E-02	5.6E-05	5.6E-05	5.6E-05	2.0E-02	2.0E-02	2.0E-04	3.8E-05	2.0E-02
Zr(IV)	2.0E-02	-	2.0E-02	-	2.0E-02	2.0E-02	-	2.0E-02	2.0E-02

Table A-23. *Best estimate K_d values (m^3/kg) for kaolinite at Olkiluoto at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	2.0E-03	2.0E-03	6.0E-04	6.0E-04	7.2E-06	6.4E-08	6.4E-08	7.2E-05	4.2E-07
Am(III)	5.0E+00	5.0E+00	4.8E+02		3.0E+02	6.0E+02		3.0E+02	3.0E+01
Be(II)	5.0E+01	5.0E+01	1.8E+02		1.8E+02	1.8E+02		1.8E+02	1.8E+02
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	3.0E-03	3.0E-03	1.0E-04		2.5E-05	2.0E-06		1.5E-04	1.5E-05
Cm(III)	5.0E+00	5.0E+00	4.8E+02		3.0E+02	6.0E+02		3.0E+02	3.0E+01
Cs(I)	2.1E-01	2.1E-01	6.0E-02		2.0E-03	4.0E-04		1.0E-02	1.0E-03
Eu(III)	5.0E+00	5.0E+00	4.8E+02		3.0E+02	6.0E+02		3.0E+02	3.0E+01
Ho(III)									
I(-I)	1.0E-01	1.0E-01	3.4E-03		8.4E-04	6.7E-05		5.0E-03	5.0E-04
Mo(VI)	1.0E-01	1.0E-01	2.9E-02		6.6E-02	4.5E-02		2.7E-02	2.7E-02
Nb(V)	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01
Ni(II)	1.0E+00	1.0E+00	5.9E+00	-	6.5E-01	5.4E+00	-	1.0E+00	3.3E-01
Np(IV)	6.0E+01	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
Np(V)		2.0E-03		2.0E-01			2.0E-02		
Pa(V)	1.5E+02	1.5E+02	1.5E+02		1.5E+02	1.5E+02		1.5E+02	1.5E+02
Pd(II)	1.0E+00	1.0E+00	5.9E+00	-	6.5E-01	5.4E+00	-	1.0E+00	3.3E-01
Pu(III)	5.0E+00	-	4.8E+02	-	3.0E+02	6.0E+02	-	3.0E+02	3.0E+01
Pu(IV)	6.0E+01	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
Pu(V,VI)	-	2.0E-03	-	2.0E-01	-	-	2.0E-02	-	-
Ra(II)	5.6E-02	5.6E-02	2.5E-02	2.5E-02	3.4E-03	3.4E-03	3.4E-03	1.3E-02	3.4E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.7E-01	8.5E-02	6.3E-02	3.2E-02	1.5E-02	2.6E-02	1.3E-02	6.3E-02	2.6E-02
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.0E+03	1.0E+03	1.0E+03		1.0E+03	1.0E+03		1.0E+03	1.0E+03
Sr(II)	5.6E-02	5.6E-02	2.5E-02	2.5E-02	3.4E-03	3.4E-03	3.4E-03	1.3E-02	3.4E-03
Tc(IV,VII)	6.0E+01	1.0E-01	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
Th(IV)	6.0E+01	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
U(IV,VI)	6.0E+01	4.7E+01	4.7E+01	4.7E+01	3.2E+01	7.2E+01	7.2E+01	3.2E+01	7.2E+01
Zr(IV)	6.0E+01	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02

Table A-24. *Best estimate K_d values (m^3/kg) for kaolinite at Olkiluoto at pH10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	2.0E-03	2.0E-03	6.0E-04	6.0E-04	7.2E-06	6.4E-08	6.4E-08	7.2E-05	4.2E-07
Am(III)	6.0E+02	6.0E+02	5.4E+02		5.4E+02	5.4E+02		9.0E+00	5.4E+02
Be(II)	1.8E+02	1.8E+02	1.8E+02		1.8E+02	1.8E+02		1.8E+02	1.8E+02
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	3.3E-05	3.3E-05	3.3E-05		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	6.0E+02	6.0E+02	5.4E+02		5.4E+02	5.4E+02		9.0E+00	5.4E+02
Cs(I)	2.1E-01	2.1E-01	6.0E-02		2.0E-03	4.0E-04		1.0E-02	1.0E-03
Eu(III)	6.0E+02	6.0E+02	5.4E+02		5.4E+02	5.4E+02		9.0E+00	5.4E+02
Ho(III)									
I(-I)	1.1E-03	1.1E-03	1.1E-03		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.5E-02	1.5E-02	1.5E-02		1.5E-02	1.5E-02		1.5E-02	1.5E-02
Nb(V)	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01	4.9E+01
Ni(II)	1.5E+01	1.5E+01	1.4E+01	-	1.4E+01	1.4E+01	-	1.3E+01	1.4E+01
Np(IV)	2.0E+02	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
Np(V)		3.0E+00		1.0E-01			3.0E+00		
Pa(V)	1.5E+02	1.5E+02	1.5E+02		1.5E+02	1.5E+02		1.5E+02	1.5E+02
Pd(II)	1.5E+01	1.5E+01	1.4E+01	-	1.4E+01	1.4E+01	-	1.3E+01	1.4E+01
Pu(III)	6.0E+02	-	5.4E+02	-	5.4E+02	5.4E+02	-	9.0E+00	5.4E+02
Pu(IV)	2.0E+02	-	2.0E+02	-	2.0E+02	2.0E+02	-	6.0E+01	2.0E+02
Pu(V,VI)	-	3.0E+00	-	1.0E-01	-	-	3.0E+00	-	-
Ra(II)	6.0E-02	6.0E-02	2.5E-02	2.5E-02	3.4E-03	3.4E-03	3.4E-03	1.3E-02	3.4E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	6.6E-02	3.3E-02	6.3E-02	3.2E-02	1.5E-02	1.1E-02	5.5E-03	6.3E-02	1.1E-02
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.0E+02	1.0E+02	1.0E+02		1.0E+02	1.0E+02		1.0E+02	1.0E+02
Sr(II)	6.0E-02	6.0E-02	2.5E-02	2.5E-02	3.4E-03	3.4E-03	3.4E-03	1.3E-02	3.4E-03
Tc(IV,VII)	2.0E+02	1.1E-03	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
Th(IV)	2.0E+02	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02
U(IV,VI)	2.0E+02	4.7E+01	4.7E+01	4.7E+01	3.2E+01	7.2E+01	7.2E+01	3.2E+01	7.2E+01
Zr(IV)	2.0E+02	-	2.0E+02	-	2.0E+02	2.0E+02	-	2.0E+02	2.0E+02

Table A-25. *Best estimate K_d values (m^3/kg) for illite at Olkiluoto at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	6.7E-03	6.7E-03	2.1E-03	2.1E-03	2.4E-05	2.1E-07	2.1E-07	2.4E-04	1.4E-06
Am(III)	1.0E+02	1.0E+02	2.0E+02		2.5E+02	2.5E+02		2.5E+02	2.5E+02
Be(II)	5.0E+01	5.0E+01	1.8E+02		1.8E+02	1.8E+02		1.8E+02	1.8E+02
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, $-CO_2H$									
Cl(-I)	1.2E-03	1.2E-03	4.0E-05		1.0E-05	8.0E-07		6.0E-05	6.0E-06
Cm(III)	1.0E+02	1.0E+02	2.0E+02		2.5E+02	2.5E+02		2.5E+02	2.5E+02
Cs(I)	1.3E+01	1.3E+01	7.8E+00		7.5E+00	7.5E+00		7.5E+00	7.3E+00
Eu(III)	1.0E+02	1.0E+02	2.0E+02		2.5E+02	2.5E+02		2.5E+02	2.5E+02
Ho(III)									
I(-I)	3.6E-03	3.6E-03	1.2E-04		3.5E-05	2.4E-06		1.8E-04	1.8E-05
Mo(VI)	1.7E-01	1.7E-01	3.4E-02		1.5E-02	5.0E-03		5.0E-02	2.8E-02
Nb(V)	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00
Ni(II)	7.0E+00	7.0E+00	1.2E+01	-	9.0E+00	9.3E+00	-	8.1E+00	9.4E+00
Np(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
Np(V)		1.4E-02		5.0E-02			1.6E-02		
Pa(V)	6.0E+01	6.0E+01	6.0E+01		6.0E+01	6.0E+01		6.0E+01	6.0E+01
Pd(II)	7.0E+00	7.0E+00	1.2E+01	-	9.0E+00	9.3E+00	-	8.1E+00	9.4E+00
Pu(III)	1.0E+02	-	2.0E+02	-	2.5E+02	2.5E+02	-	2.5E+02	2.5E+02
Pu(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
Pu(V,VI)	-	1.4E-02	-	5.0E-02	-	-	1.6E-02	-	-
Ra(II)	7.8E+00	7.8E+00	1.9E-01	1.9E-01	2.3E-02	6.6E-04	6.6E-04	5.8E-02	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	4.0E-03	2.0E-03	1.2E-02	6.0E-03	1.3E-02	3.6E-02	1.8E-02	1.2E-02	3.6E-02
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.5E+02	1.5E+02	1.5E+02		1.5E+02	1.5E+02		1.5E+02	1.5E+02
Sr(II)	7.8E+00	7.8E+00	1.9E-01	1.9E-01	2.3E-02	6.6E-04	6.6E-04	5.8E-02	2.0E-03
Tc(IV,VII)	2.0E+01	3.6E-03	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
Th(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
U(IV,VI)	2.0E+01	1.9E+01	1.9E+01	1.9E+01	1.3E+01	8.4E+01	8.4E+01	1.3E+01	8.4E+01
Zr(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01

Table A-26. *Best estimate K_d values (m^3/kg) for illite at Olkiluoto at pH10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	6.7E-03	6.7E-03	2.1E-03	2.1E-03	2.4E-05	2.1E-07	2.1E-07	2.4E-04	1.4E-06
Am(III)	2.5E+02	2.5E+02	2.3E+02		2.3E+02	2.3E+02		4.0E+00	2.3E+02
Be(II)	1.8E+02	1.8E+02	1.8E+02		1.8E+02	1.8E+02		1.8E+02	1.8E+02
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	1.3E-05	1.3E-05	1.3E-05		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	2.5E+02	2.5E+02	2.3E+02		2.3E+02	2.3E+02		4.0E+00	2.3E+02
Cs(I)	1.3E+01	1.3E+01	7.8E+00		7.5E+00	7.5E+00		7.5E+00	7.3E+00
Eu(III)	2.5E+02	2.5E+02	2.3E+02		2.3E+02	2.3E+02		4.0E+00	2.3E+02
Ho(III)									
I(-I)	4.0E-05	4.0E-05	4.0E-05		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.0E-02	1.0E-02	1.0E-02		1.8E-04	1.8E-04		1.0E-02	1.8E-04
Nb(V)	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00	4.5E+00
Ni(II)	1.6E+01	1.6E+01	1.5E+01	-	9.9E+00	9.9E+00	-	8.8E+00	9.9E+00
Np(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
Np(V)		1.0E+00		4.0E-02			1.0E+00		
Pa(V)	6.0E+01	6.0E+01	6.0E+01		6.0E+01	6.0E+01		6.0E+01	6.0E+01
Pd(II)	1.6E+01	1.6E+01	1.5E+01	-	9.9E+00	9.9E+00	-	8.8E+00	9.9E+00
Pu(III)	2.5E+02	-	2.3E+02	-	2.3E+02	2.3E+02	-	4.0E+00	2.3E+02
Pu(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	6.0E+00	2.0E+01
Pu(V,VI)	-	1.0E+00	-	4.0E-02	-	-	1.0E+00	-	-
Ra(II)	7.8E+00	7.8E+00	1.9E-01	1.9E-01	2.3E-02	6.6E-04	6.6E-04	5.8E-02	2.0E-03
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	4.0E-04	2.0E-04	1.2E-02	6.0E-03	2.3E-03	8.3E-03	4.2E-03	1.2E-02	8.3E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	9.0E+01	9.0E+01	9.0E+01		9.0E+01	9.0E+01		9.0E+01	9.0E+01
Sr(II)	7.8E+00	7.8E+00	1.9E-01	1.9E-01	2.3E-02	6.6E-04	6.6E-04	5.8E-02	2.0E-03
Tc(IV,VII)	2.0E+01	4.0E-05	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
Th(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01
U(IV,VI)	2.0E+01	1.9E+01	1.9E+01	1.9E+01	1.3E+01	8.4E+01	8.4E+01	1.3E+01	8.4E+01
Zr(IV)	2.0E+01	-	2.0E+01	-	2.0E+01	2.0E+01	-	2.0E+01	2.0E+01

Table A-27. *Lower limit K_d values (m^3/kg) for kaolinite at Olkiluoto at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	4.5E-04	4.5E-04	1.4E-04	1.4E-04	1.6E-06	1.4E-08	1.4E-08	1.6E-05	9.4E-08
Am(III)	2.4E-01	2.4E-01	5.3E+01		1.4E+01	6.6E+01		1.4E+01	1.0E+00
Be(II)	9.1E-02	9.1E-02	5.9E-01		6.5E-02	5.4E-01		1.0E-01	3.3E-02
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, $-CO_2H$									
Cl(-I)	2.0E-04	2.0E-04	6.7E-06		1.7E-06	1.3E-07		1.0E-05	1.0E-06
Cm(III)	2.4E-01	2.4E-01	5.3E+01		1.4E+01	6.6E+01		1.4E+01	1.0E+00
Cs(I)	4.0E-02	4.0E-02	1.1E-02		3.6E-04	7.1E-05		1.8E-03	1.8E-04
Eu(III)	2.4E-01	2.4E-01	5.3E+01		1.4E+01	6.6E+01		1.4E+01	1.0E+00
Ho(III)									
I(-I)	6.7E-03	6.7E-03	2.3E-04		5.6E-05	4.5E-06		3.3E-04	3.3E-05
Mo(VI)	8.3E-03	8.3E-03	2.4E-03		5.5E-03	7.5E-03		2.3E-03	2.3E-03
Nb(V)	1.6E+01	1.6E+01	2.2E+01	1.6E+01	2.2E+01	2.2E+01	1.6E+01	1.6E+01	1.6E+01
Ni(II)	9.1E-02	9.1E-02	5.9E-01	-	6.5E-02	5.4E-01	-	1.0E-01	3.3E-02
Np(IV)	2.7E+01	-	8.4E+01	-	8.3E+01	8.4E+01	-	6.0E+01	6.0E+01
Np(V)		2.0E-04		2.0E-02			2.0E-03		
Pa(V)	2.8E+01	2.8E+01	2.8E+01		2.8E+01	4.0E+01		2.8E+01	2.8E+01
Pd(II)	9.1E-02	9.1E-02	5.9E-01	-	6.5E-02	5.4E-01	-	1.0E-01	3.3E-02
Pu(III)	2.4E-01	-	5.3E+01	-	1.4E+01	6.6E+01	-	1.4E+01	1.0E+00
Pu(IV)	2.7E+01	-	8.4E+01	-	8.3E+01	8.4E+01	-	6.0E+01	6.0E+01
Pu(V,VI)	-	2.0E-04	-	2.0E-02	-	-	2.0E-03	-	-
Ra(II)	1.1E-02	1.1E-02	1.8E-02	1.8E-02	3.0E-04	3.0E-04	3.0E-04	1.2E-03	3.0E-04
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	8.3E-02	2.1E-02	3.1E-02	8.0E-03	7.0E-03	4.9E-03	3.8E-03	1.6E-02	3.5E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.3E+02	1.3E+02	1.4E+02		1.0E+02	1.0E+02		1.0E+02	1.0E+02
Sr(II)	1.1E-02	1.1E-02	1.8E-02	1.8E-02	3.0E-04	3.0E-04	3.0E-04	1.2E-03	3.0E-04
Tc(IV,VII)	2.7E+01	6.7E-03	8.4E+01	-	8.3E+01	8.4E+01	-	6.0E+01	6.0E+01
Th(IV)	2.7E+01	-	8.4E+01	-	8.3E+01	8.4E+01	-	6.0E+01	6.0E+01
U(IV,VI)	2.0E+01	1.3E+01	1.9E+01	1.3E+01	2.7E+00	1.1E+01	1.8E+01	9.0E+00	2.2E+01
Zr(IV)	2.7E+01	-	8.4E+01	-	8.3E+01	8.4E+01	-	6.0E+01	6.0E+01

Table A-28. *Lower limit K_d values (m^3/kg) for kaolinite at Olkiluoto at pH10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	4.5E-04	4.5E-04	1.4E-04	1.4E-04	1.6E-06	1.4E-08	1.4E-08	1.6E-05	9.4E-08
Am(III)	2.9E+01	2.9E+01	5.9E+01		2.6E+01	5.9E+01		4.3E-01	2.6E+01
Be(II)	1.4E+00	1.4E+00	1.4E+00		1.4E+00	1.4E+00		1.3E+00	1.4E+00
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	2.2E-06	2.2E-06	2.2E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	2.9E+01	2.9E+01	5.9E+01		2.6E+01	5.9E+01		4.3E-01	2.6E+01
Cs(I)	4.0E-02	4.0E-02	1.1E-02		3.6E-04	7.1E-05		1.8E-03	1.8E-04
Eu(III)	2.9E+01	2.9E+01	5.9E+01		2.6E+01	5.9E+01		4.3E-01	2.6E+01
Ho(III)									
I(-I)	7.3E-5	7.3E-5	7.3E-5		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	1.3E-03	1.3E-03	1.3E-03		1.3E-03	2.5E-03		1.3E-03	1.3E-03
Nb(V)	2.2E+01	1.6E+01	2.2E+01	1.6E+01	1.6E+01	2.2E+01	1.6E+01	1.6E+01	1.6E+01
Ni(II)	1.4E+00	1.4E+00	1.4E+00	-	1.4E+00	1.4E+00	-	1.3E+00	1.4E+00
Np(IV)	8.4E+01	-	8.4E+01	-	8.4E+01	8.4E+01	-	6.0E+01	6.0E+01
Np(V)		3.0E-01		1.0E-02			3.0E-01		
Pa(V)	2.8E+01	2.8E+01	2.8E+01		2.8E+01	4.0E+01		2.8E+01	2.8E+01
Pd(II)	1.4E+00	1.4E+00	1.4E+00	-	1.4E+00	1.4E+00	-	1.3E+00	1.4E+00
Pu(III)	2.9E+01	-	5.9E+01	-	2.6E+01	5.9E+01	-	4.3E-01	2.6E+01
Pu(IV)	8.4E+01	-	8.4E+01	-	8.4E+01	8.4E+01	-	2.5E+01	6.0E+01
Pu(V,VI)	-	3.0E-01	-	1.0E-02	-	-	3.0E-01	-	-
Ra(II)	1.1E-02	1.8E-02	1.8E-02	1.8E-02	3.0E-04	3.0E-04	3.0E-04	1.2E-03	3.0E-04
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	2.4E-02	8.3E-03	2.2E-02	8.0E-03	5.2E-03	1.7E-03	8.7E-04	1.6E-02	1.7E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.3E+01	1.3E+01	1.4E+01		1.0E+01	1.0E+01		1.0E+01	1.0E+01
Sr(II)	1.1E-02	1.8E-02	1.8E-02	1.8E-02	3.0E-04	3.0E-04	3.0E-04	1.2E-03	3.0E-04
Tc(IV,VII)	8.2E+01	7.3E-05	8.4E+01	-	8.4E+01	8.4E+01	-	6.0E+01	6.0E+01
Th(IV)	8.4E+01	-	8.4E+01	-	8.4E+01	8.4E+01	-	6.0E+01	6.0E+01
U(IV,VI)	8.4E+01	1.3E+01	1.9E+01	1.3E+01	3.8E+01	1.1E+01	1.8E+01	9.0E+00	2.2E+01
Zr(IV)	8.4E+01	-	8.4E+01	-	8.4E+01	8.4E+01	-	6.0E+01	6.0E+01

Table A-29. *Lower limit K_d values (m^3/kg) for illite at Olkiluoto at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	1.2E-03	1.2E-03	3.6E-04	3.6E-04	4.1E-06	3.6E-08	3.6E-08	4.1E-05	2.4E-07
Am(III)	1.1E+01	1.1E+01	3.7E+01		2.1E+01	4.6E+01		2.1E+01	1.3E+01
Be(II)	4.7E-01	4.7E-01	1.1E+00		6.0E-01	8.5E-01		5.4E-01	6.3E-01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	4.6E-05	4.6E-05	1.5E-06		3.9E-07	3.9E-07		2.3E-06	2.3E-07
Cm(III)	1.1E+01	1.1E+01	3.7E+01		2.1E+01	4.6E+01		2.1E+01	1.3E+01
Cs(I)	1.8E+00	1.8E+00	1.1E+00		1.0E+00	1.0E+00		1.0E+00	1.0E+00
Eu(III)	1.1E+01	1.1E+01	3.7E+01		2.1E+01	4.6E+01		2.1E+01	1.3E+01
Ho(III)									
I(-I)	1.4E-04	1.4E-04	4.6E-06		1.4E-06	9.2E-08		6.9E-06	6.9E-07
Mo(VI)	1.1E-02	1.1E-02	4.3E-03		1.0E-03	6.3E-04		3.3E-03	1.9E-03
Nb(V)	5.9E-01	5.9E-01	8.2E-01	5.9E-01	8.2E-01	8.2E-01	5.9E-01	5.9E-01	5.9E-01
Ni(II)	4.7E-01	4.7E-01	1.1E+00	-	6.0E-01	8.5E-01	-	5.4E-01	6.3E-01
Np(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
Np(V)		1.0E-03		4.0E-03			1.0E-03		
Pa(V)	5.5E+00	5.5E+00	7.7E+00		5.5E+00	5.5E+00		5.5E+00	5.5E+00
Pd(II)	4.7E-01	4.7E-01	1.1E+00	-	6.0E-01	8.5E-01	-	5.4E-01	6.3E-01
Pu(III)	1.1E+01	-	3.7E+01	-	2.1E+01	4.6E+01	-	2.1E+01	1.3E+01
Pu(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
Pu(V,VI)	-	1.0E-03	-	4.0E-03	-	-	1.0E-03	-	-
Ra(II)	5.4E-01	5.4E-01	1.3E-02	1.3E-02	1.6E-03	4.5E-05	4.5E-05	4.0E-03	1.4E-04
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.5E-03	3.8E-04	3.3E-03	1.2E-03	5.0E-03	2.7E-03	3.1E-03	2.3E-03	2.7E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	2.9E+01	2.9E+01	4.2E+01		2.9E+01	2.9E+01		2.9E+01	2.9E+01
Sr(II)	5.4E-01	5.4E-01	1.3E-02	1.3E-02	1.6E-03	4.5E-05	4.5E-05	4.0E-03	1.4E-04
Tc(IV,VII)	7.5E+00	1.4E-04	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
Th(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
U(IV,VI)	7.5E+00	4.7E+00	6.4E+00	4.7E+00	4.9E+00	3.1E+01	1.5E+01	3.3E+00	3.1E+01
Zr(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00

Table A-30. *Lower limit K_d values (m^3/kg) for illite at Olkiluoto at pH10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	1.2E-03	1.2E-03	3.6E-04	3.6E-04	4.1E-06	3.6E-08	3.6E-08	4.1E-05	2.4E-07
Am(III)	2.1E+01	2.1E+01	4.2E+01		1.9E+01	4.2E+01		3.3E-01	1.9E+01
Be(II)	1.1E+00	1.1E+00	1.4E+00		6.6E-01	9.0E-01		5.9E-01	6.6E-01
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)	5.0E-07	5.0E-07	5.0E-07		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Cm(III)	2.1E+01	2.1E+01	4.2E+01		1.9E+01	4.2E+01		3.3E-01	1.9E+01
Cs(I)	1.8E+00	1.8E+00	1.1E+00		1.0E+00	1.0E+00		1.0E+00	1.0E+00
Eu(III)	2.1E+01	2.1E+01	4.2E+01		1.9E+01	4.2E+01		3.3E-01	1.9E+01
Ho(III)									
I(-I)	1.5E-06	1.5E-06	1.5E-06		0.0E+00	0.0E+00		0.0E+00	0.0E+00
Mo(VI)	6.7E-04	6.7E-04	1.3E-03		1.2E-05	2.3E-05		6.7E-04	1.2E-05
Nb(V)	8.2E-01	5.9E-01	8.2E-01	5.9E-01	5.9E-01	8.2E-01	5.9E-01	5.9E-01	5.9E-01
Ni(II)	1.1E+00	1.1E+00	1.4E+00	-	6.6E-01	9.0E-01	-	5.9E-01	6.6E-01
Np(IV)	7.5E+00	-	7.5E+00	--	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
Np(V)		1.0E-01		3.0E-03			1.0E-01		
Pa(V)	5.5E+00	5.5E+00	7.7E+00		5.5E+00	5.5E+00		5.5E+00	5.5E+00
Pd(II)	1.1E+00	1.1E+00	1.4E+00	-	6.6E-01	9.0E-01	-	5.9E-01	6.6E-01
Pu(III)	2.1E+01	-	4.2E+01	-	1.9E+01	4.2E+01	-	3.3E-01	1.9E+01
Pu(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	2.3E+00	5.3E+00
Pu(V,VI)	-	1.0E-01	-	3.0E-03	-	-	1.0E-01	-	-
Ra(II)	5.4E-01	5.4E-01	1.3E-02	1.3E-02	1.6E-03	4.5E-05	4.5E-05	4.0E-03	1.4E-04
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	4.9E-05	3.8E-05	3.3E-03	1.2E-03	6.2E-04	1.0E-03	5.1E-04	2.3E-03	1.0E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	1.2E+01	1.2E+01	1.6E+01		1.2E+01	1.2E+01		1.2E+01	1.2E+01
Sr(II)	5.4E-01	5.4E-01	1.3E-02	1.3E-02	1.6E-03	4.5E-05	4.5E-05	4.0E-03	1.4E-04
Tc(IV,VII)	7.3E+00	1.5E-06	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
Th(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00
U(IV,VI)	7.5E+00	4.7E+00	6.4E+00	4.7E+00	4.9E+00	3.1E+01	1.5E+01	3.3E+00	3.1E+01
Zr(IV)	7.5E+00	-	7.5E+00	-	7.5E+00	7.5E+00	-	5.3E+00	5.3E+00

Table A-31. *Best estimate K_d values (m^3/kg) for chlorite at Olkiluoto at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	-	-	-	-	-	-	-	-	-
Am(III)									
Be(II)									
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)									
Cm(III)									
Cs(I)									
Eu(III)									
Ho(III)									
I(-I)									
Mo(VI)									
Nb(V)	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01
Ni(II)									
Np(IV)									
Np(V)									
Pa(V)									
Pd(II)	-	-	-	-	-	-	-	-	-
Pu(III)	-	-	-	-	-	-	-	-	-
Pu(IV)	-	-	-	-	-	-	-	-	-
Pu(V,VI)	-	-	-	-	-	-	-	-	-
Ra(II)	-	-	-	-	-	-	-	-	-
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.5E-01	7.5E-02	1.5E-01	7.5E-02	2.4E-02	2.1E-02	1.1E-02	1.5E-01	2.1E-02
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	2.3E+02	2.3E+02	6.0E+01		1.8E+02	1.0E+02		2.0E+02	1.1E+02
Sr(II)	-	-	-	-	-	-	-	-	-
Tc(IV,VII)	-	-	-	-	-	-	-	-	-
Th(IV)	1.0E+02	-	3.0E+02	-	3.0E+02	3.0E+02	-	3.0E+02	3.0E+02
U(IV,VI)	-	-	-	-	-	-	-	-	-
Zr(IV)	-	-	-	-	-	-	-	-	-

Table A-32. *Best estimate K_d values (m^3/kg) for chlorite at Olkiluoto at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	-	-	-	-	-	-	-	-	-
Am(III)									
Be(II)									
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, $-CO_2H$									
Cl(-I)									
Cm(III)									
Cs(I)									
Eu(III)									
Ho(III)									
I(-I)									
Mo(VI)									
Nb(V)	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01	3.4E+01
Ni(II)									
Np(IV)									
Np(V)									
Pa(V)									
Pd(II)	-	-	-	-	-	-	-	-	-
Pu(III)	-	-	-	-	-	-	-	-	-
Pu(IV)	-	-	-	-	-	-	-	-	-
Pu(V,VI	-	-	-	-	-	-	-	-	-
Ra(II)	-	-	-	-	-	-	-	-	-
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	1.5E-01	7.5E-02	3.1E-02	1.6E-02	2.4E-02	2.1E-02	1.1E-02	3.1E-02	2.1E-02
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	2.5E+01	2.5E+01	9.1E+00		2.0E+01	1.1E+01		2.2E+01	1.2E+01
Sr(II)	-	-	-	-	-	-	-	-	-
Tc(IV,VII)	-	-	-	-	-	-	-	-	-
Th(IV)	3.0E+02	-	3.0E+02	-	3.0E+02	3.0E+02	-	3.0E+02	3.0E+02
U(IV,VI)	-	-	-	-	-	-	-	-	-
Zr(IV)	-	-	-	-	-	-	-	-	-

Table A-33. *Lower limit K_d values (m^3/kg) for chlorite at Olkiluoto at the pH of reference water (REF). Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

REF pH	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	-	-	-	-	-	-	-	-	-
Am(III)									
Be(II)									
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)									
Cm(III)									
Cs(I)									
Eu(III)									
Ho(III)									
I(-I)									
Mo(VI)									
Nb(V)	4.5E+00	4.5E+00	6.2E+00	4.5E+00	6.2E+00	6.2E+00	4.5E+00	4.5E+00	4.5E+00
Ni(II)									
Np(IV)									
Np(V)									
Pa(V)									
Pd(II)	-	-	-	-	-	-	-	-	-
Pu(III)									
Pu(IV)									
Pu(V,VI)									
Ra(II)	-	-	-	-	-	-	-	-	-
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	4.1E-02	1.4E-02	5.8E-02	1.4E-02	9.2E-03	2.2E-03	1.9E-03	2.9E-02	1.6E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	2.5E+01	2.5E+01	9.1E+00		2.0E+01	1.1E+01		2.2E+01	1.2E+01
Sr(II)	-	-	-	-	-	-	-	-	-
Tc(IV,VII)	-	-	-	-	-	-	-	-	-
Th(IV)	3.5E+01	-	9.9E+01	-	9.9E+01	9.9E+01	-	7.0E+01	7.0E+01
U(IV,VI)	-	-	-	-	-	-	-	-	-
Zr(IV)	-	-	-	-	-	-	-	-	-

Table A-34. *Lower limit K_d values (m^3/kg) for chlorite at Olkiluoto at pH 10. Waters KR4 = KR4_81_1; KR20 = KR20_465_1. Elements not considered are marked in italics.*

pH 10	OLGA	OLGO	ALLMR	ALLMO	OLBA	OLSR	OLSO	KR4	KR20
Ag(I)	-	-	-	-	-	-	-	-	-
Am(III)									
Be(II)									
C_{inorg}	-	-	-	-	-	-	-	-	-
C, CH_4									
C, -CO_2H									
Cl(-I)									
Cm(III)									
Cs(I)									
Eu(III)									
Ho(III)									
I(-I)									
Mo(VI)									
Nb(V)	6.2E+00	4.5E+00	6.2E+00	4.5E+00	4.5E+00	6.2E+00	4.5E+00	4.5E+00	4.5E+00
Ni(II)									
Np(IV)									
Np(V)									
Pa(V)									
Pd(II)	-	-	-	-	-	-	-	-	-
Pu(III)									
Pu(IV)									
Pu(V,VI)									
Ra(II)	-	-	-	-	-	-	-	-	-
Se(-II)	-	-	-	-	-	-	-	-	-
Se (IV)	2.6E-02	1.4E-02	8.5E-03	3.1E-03	6.5E-03	2.5E-03	1.3E-03	6.0E-03	2.5E-03
Se(VI)	-	-	-	-	-	-	-	-	-
Sm(III)									
Sn(IV)	3.3E+00	3.3E+00	4.5E+00		3.3E+00	3.3E+00		3.3E+00	3.3E+00
Sr(II)	-	-	-	-	-	-	-	-	-
Tc(IV,VII)	-	-	-	-	-	-	-	-	-
Th(IV)	9.9E+01	-	9.9E+01	-	9.9E+01	9.9E+01	-	7.0E+01	7.0E+01
U(IV,VI)	-	-	-	-	-	-	-	-	-
Zr(IV)	-	-	-	-	-	-	-	-	-

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